

Relativistic Magnetohydrodynamics

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Starting with the relativistic Boltzmann transport equation, basic equations for relativistic magnetohydrodynamics of perfect and imperfect gases are derived. Relativistic magnetohydrodynamical generalizations of Kelvin's circulation theorem, Helmholtz's vortex theorem and Rankine-Hugoniot's shock relations for the simple gas are also given.

§ 1. Introduction

In the recent striking progress in plasma physics, it is sometimes required to treat charged particle streams with very high speeds or with very strong magnetic fields. In this paper we will give a relativistic generalization of magnetohydrodynamics throughout in a covariant manner.

Relativistic generalizations of ordinary hydrodynamics were performed by Eckart,¹⁾ Taub²⁾ and Synge.³⁾ By combining these methods we will take here a method which is completely covariant and convenient for a physical interpretation. Though relativistic invariance of the distribution function has been discussed by several authors, a direct covariant treatment of the relativistic Boltzmann equation is attempted in § 2. Starting with this equation, relativistic mean value equations are given in § 3 particularly for a simple fluid with the method used by Eckart and Taub. Basic equations describing a fully ionized fluid and a partially ionized fluid are given in § 4 and § 5 respectively.

The relativistic generalization of Kelvin's circulation theorem of ordinary hydrodynamics was performed by Frankl,⁴⁾ and we have been told recently that a generalization of the vortex theorem was also performed by G. Iwata for magnetohydrodynamics with the method of Synge. Since the Lorentz force is not a conservative force, the ordinary circulation and vortex theorems do not hold. But a conservation theorem holds with respect to a certain quantity generalized from the ordinary one. The constants appearing in the relativistic magnetohydrodynamical generalizations of circulation and vortex theorems are not formal four-dimensional generalizations of the ordinary expressions of the circulation and the vorticity. This will be treated in § 6.

Generalizations of Rankine-Hugoniot's shock relations are performed by Taub²⁾ for the relativistic case and by de Hoffmann and Teller⁵⁾ for the magnetohydrodynamical case. In § 7 shock conditions in a one-dimensional flow of a simple fluid in a uniform electromagnetic field are given in a somewhat general form by using the method of de Hoffmann and Teller. But generalizations of the vortex theorem and the shock relations to the nonsimple gases such as a neutral gas plasma are not yet accomplished.

§ 2. The relativistic Boltzmann equation

Let us consider the relativistic transport phenomena in the Minkowski space with the coordinates

$$x^1 = x, \quad x^2 = y, \quad x^3 = z, \quad x^4 = ct$$

and the metric

$$g^{11} = g^{22} = g^{33} = -g^{44} = 1, \quad g^{\alpha\beta} = 0 \quad (\alpha \neq \beta). \quad (2.1)$$

We use Latin letters $k, l, \dots$ for the space indices 1, 2, 3, Greek letters $\alpha, \beta, \dots$ for the space-time indices 1, 2, 3, 4 and the usual summation convention with respect to the doubled indices.

The four-velocity is defined by

$$u^i = (1 - \beta^2)^{-1/2} c^{-1} dx^i / dt, \quad u^4 = (1 - \beta^2)^{-1/2},$$

$$\beta^2 = c^{-2} ((dx^1/dt)^2 + (dx^2/dt)^2 + (dx^3/dt)^2) \quad (2.2)$$

and they satisfy the identical relation

$$u^\alpha u_\alpha = -1. \quad (2.3)$$

The direction of the velocity u^α means the direction of the particle path in the four dimensional world and a component of a vector of time like length $d\tau$ in this direction is $u^\alpha d\tau$, whose squared length is indeed given by (2.3) as

$$(u^\alpha d\tau)(u_\alpha d\tau) = -d\tau^2. \quad (2.4)$$

Hereafter we use $c\tau$ as a parameter denoting the invariant length along the world line or the proper time. Using the velocity vector we can introduce a symmetric tensor by

$$s^{\alpha\beta} = g^{\alpha\beta} + u^\alpha u^\beta, \quad (2.5)$$

which is orthogonal to the direction of the particle path, for

$$u_\alpha s^{\alpha\beta} = u_\alpha (g^{\alpha\beta} + u^\alpha u^\beta) = 0. \quad (2.6)$$

So it can be interpreted as lying in the proper space direction.

On account of the restriction (2.3), the velocity space in the relativistic theory has a peculiar structure. It is a three dimensional subspace restricted by (2.3) in the four dimensional space with the Minkowskian structure, having the invariant volume element

$$dU = du^1 du^2 du^3 / u^4 = (1 + u^i u_i)^{-1/2} d^3 u, \quad (2.7)$$

where

$$d^3 u = du^1 du^2 du^3. \quad (2.8)$$

As discussed in detail by Synge and others, the concept of the number of particles occupying the invariant volume element fdU is relativistically invariant. So the distribution function $f(x^\alpha, u^\alpha)$ has an invariant meaning. Since the equations of motion for a particle with rest mass m_0 and charge e in an external electromagnetic field $F_{\alpha\beta} = \partial_\alpha A_\beta - \partial_\beta A_\alpha$ is

$$cm_0 \cdot du^\alpha/d\tau = F^\alpha, \quad F^\alpha = eu_\beta F^{\alpha\beta}, \quad (2.9)$$

$$1/c \cdot dx^\alpha/d\tau = u^\alpha,$$

the rate of change of f during $dt = c^{-1}u^4 d\tau$ is

$$\{f(x^\alpha + cu^\alpha d\tau, u^\alpha + c^{-1}m_0^{-1}F^\alpha d\tau) - f(x^\alpha, u^\alpha)\} / dt$$

$$= (cu^\alpha \cdot \partial f / \partial x^\alpha + c^{-1}m_0^{-1}F^\alpha \cdot \partial f / \partial u^\alpha) \cdot c / u^4. \quad (2.10)$$

If the rate of change of f due to collisions is denoted by $\Delta'_{\text{col}} f$, the relativistic form of Boltzmann's transport equation is

$$cu^\alpha \cdot \partial f / \partial x^\alpha + c^{-1}m_0^{-1}F^\alpha \cdot \partial f / \partial u^\alpha = c^{-1}u^4 \Delta'_{\text{col}} f = \Delta_{\text{col}} f, \quad (2.11)$$

where $\Delta_{\text{col}} = c^{-1}u^4 \Delta'_{\text{col}}$ is the invariant collision operator.

Now let us show that this relativistic equation is equivalent to the ordinary Boltzmann equation. Since the number of independent variables is three, we can regard u^i as the independent variables and u^4 as a function of them. In this case the distribution function can be expressed as $f^*(x^\alpha, u^i) = f(x^\alpha, u^\alpha)$. Since u^4 is a dependent variable,

$$F^i \frac{\partial f^*(x^\alpha, u^i)}{\partial u^i} = F^i \left(\frac{\partial f(x^\alpha, u^\alpha)}{\partial u^i} + \frac{\partial u^4}{\partial u^i} \frac{\partial f(x^\alpha, u^\alpha)}{\partial u^4} \right)$$

$$= F^i \cdot \partial f / \partial u^i + F^i \cdot u^i / u^4 \cdot \partial f / \partial u^4$$

$$= F^i \cdot \partial f / \partial u^i + F^4 \cdot \partial f / \partial u^4$$

$$= F^\alpha \cdot \partial f / \partial u^\alpha, \quad (2.12)$$

where we used the well-known identical relation among the components of the four-force

$$u_\alpha F^\alpha = 0. \quad (2.13)$$

Therefore the equation (2.11) reduces to the familiar form

$$cu^\alpha \cdot \partial f^* / \partial x^\alpha + c^{-1}m_0^{-1}F^i \cdot \partial f^* / \partial u^i = \Delta_{\text{col}} f^*. \quad (2.14)$$

Thus we have verified that (2.14) is equivalent to (2.11). This is also a verification of the relativistic invariance of the ordinary form (2.14), though it is not written in a completely covariant form. Since only independent variables appear in the equation (2.14), it is sometimes more convenient particularly for integral calculations and we will use it in some cases hereafter. If we use the asterisk generally in the same meaning as above introduced for f , the relation (2.12) holds for any function $\varphi(x^\alpha, u^\alpha) = \varphi^*(x^\alpha, u^i)$.

$$F^i \cdot \partial \varphi^* / \partial u^i = F^\alpha \cdot \partial \varphi / \partial u^\alpha. \quad (2.15)$$

§ 3. Derivation of equations for a simple gas in an external electromagnetic field

As is well known, equations for averaged quantities can be derived from the Boltzmann equation. But the method used for the ordinary hydrodynamical equation can be applied directly only for the case of the force independent of velocities. Though the magnetic

force depends upon the velocity, it has been shown that it can be applied also to an external magnetic force in the nonrelativistic theory. We can show that this holds also for the relativistic case.

Since the distribution function f is assumed as a well integrable function, for a function $\varphi(x^\alpha, u^\alpha)$ and the external Lorentz force $F^\alpha(x^\alpha, u^\alpha) = u_\beta F^{\alpha\beta}(x)$ we can easily prove the relations

$$\int \varphi u^\alpha \frac{\partial f}{\partial x^\alpha} dU = \frac{\partial}{\partial x^\alpha} \int f \varphi u^\alpha dU - \int f u^\alpha \frac{\partial \varphi}{\partial x^\alpha} dU, \quad (3.1)$$

$$\int \varphi F^\alpha \frac{\partial f}{\partial u^\alpha} dU = - \int f F^\alpha \frac{\partial \varphi}{\partial u^\alpha} dU. \quad (3.2)$$

The relation (3.2) is verified as follows,

$$\begin{aligned} \int \varphi^* F^i \frac{\partial f^*}{\partial u^i} \frac{d^3 u}{(1+u^i u_i)^{1/2}} &= - \int f^* \frac{\partial}{\partial u^i} \left(\varphi^* \frac{F^i}{(1+u^i u_i)^{1/2}} \right) d^3 u \\ &= - \int f^* F^i \frac{\partial \varphi^*}{\partial u^i} \frac{d^3 u}{(1+u^i u_i)^{1/2}} - \int f^* \varphi^* \frac{\partial}{\partial u^i} \left(\frac{F^i}{(1+u^i u_i)^{1/2}} \right) d^3 u \\ &= - \int f^* F^i \frac{\partial \varphi^*}{\partial u^i} dU, \end{aligned} \quad (3.3)$$

because

$$\frac{\partial}{\partial u^i} \left(\frac{u_\alpha F^{\alpha i}(x)}{(1+u^i u_i)^{1/2}} \right) = \frac{\partial}{\partial u^i} \left(\frac{u_i F^{ii}(x)}{(1+u^i u_i)^{1/2}} \right) = 0. \quad (3.4)$$

In the usual case,⁽¹⁾ when the function φ means a conserved quantity in collisions the collision term in the Boltzmann equation vanishes:

$$\int \varphi \mathcal{A}_{\text{col}} f dU = 0. \quad (3.5)$$

Assuming that this holds also in the relativistic case, for such a function φ we can derive the following mean value equation,

$$\frac{\partial}{\partial x^\alpha} \int f \varphi u^\alpha dU - \int f \varphi \frac{\partial (\varphi u^\alpha)}{\partial x^\alpha} dU - \int f c^{-1} m_0^{-1} F^\alpha \frac{\partial \varphi}{\partial u^\alpha} dU = 0, \quad (3.6)$$

by multiplying φ by the Boltzmann equation, integrating over all the velocity space and using the relations (3.1) and (3.2).

Since the rest mass is a collision invariant, setting $\varphi = m_0$ in (3.6) we have

$$\partial / \partial x^\alpha \cdot \int f m_0 u^\alpha dU = 0. \quad (3.7)$$

In order to express this equation in terms of quantities of the mean flow, we first consider the mean flow velocity. Though the transformation character of the four velocity is of a vector, its geometrical meaning is the direction cosine of the world line and it is a dimensionless quantity. So we may define the mean flow velocity as the direction cosine

of the mean world line, so to say, of the particle world lines, namely of a line drawn in the direction in which the particle world lines are the most dense. Thus it can be defined as the direction cosine of such a vector whose components are the mean values of particle velocity components $\bar{u}^\alpha$, where the bar stands for the mean value

$$\bar{A} = 1/n \cdot \int f A dU \quad (3.8)$$

and

$$n = \int f dU \quad (3.9)$$

is the invariant mean particle number in unit proper volume. If we denote the length and components of the line element of the world line of the mean flow by $\langle d\tau \rangle$ and $\langle dx^\alpha \rangle$ respectively, a proportional relation

$$\langle dx^\alpha \rangle / \bar{u}^\alpha = \langle d\tau \rangle / \sqrt{-\bar{u}^\alpha \bar{u}_\alpha} \quad (3.10)$$

holds and the mean flow velocity v^α becomes

$$v^\alpha = \langle dx^\alpha \rangle / \langle d\tau \rangle = \bar{u}^\alpha / \sqrt{-\bar{u}^\alpha \bar{u}_\alpha} \quad (3.11)$$

and it satisfies

$$v^\alpha v_\alpha = -1. \quad (3.12)$$

Now if we define the effective flow density ρ per unit proper volume by

$$\rho = n m_0 \sqrt{-\bar{u}^\alpha \bar{u}_\alpha}, \quad (3.13)$$

the equation (3.7) becomes

$$\partial(\rho v^\alpha) / \partial x^\alpha = 0. \quad (3.14)$$

This is the continuity equation of flow. Thus the flow behaves itself as a fluid whose density is different from the sum of the particle rest masses. The effective density occurs from the thermal motion, since setting

$$u^\alpha = \bar{u}^\alpha + u'^\alpha \quad (3.15)$$

we can easily show

$$\bar{u}^\alpha \bar{u}_\alpha = -(1 + \bar{u}'^\alpha \bar{u}'_\alpha). \quad (3.16)$$

Since the four-momentum is a collision invariant, setting $\varphi = m_0 u^\beta$ in (3.6) we have

$$\partial / \partial x^\alpha \cdot \int f m_0 c^2 u^\beta u^\alpha dU = \int f F^\beta dU. \quad (3.17)$$

This is the equation of motion, the balance of forces and the conservation of energy

$$\partial T^{\alpha\beta} / \partial x^\alpha = j_\tau F^{\beta\tau}, \quad (3.18)$$

where

$$T^{\alpha\beta} = \int f m_0 c^2 u^\alpha u^\beta dU \quad (3.19)$$

is the mean energy momentum tensor,

$$j_{\tau} = \int f e u_{\tau} dU = m_0^{-1} e \rho v_{\tau} \quad (3 \cdot 20)$$

is the mean four-current and

$$j_{\tau} F^{\beta\tau} = \int f e u_{\tau} F^{\beta\tau} dU = \int f F^{\beta} dU \quad (3 \cdot 21)$$

is the mean Lorentz force acting on unit proper volume of the fluid.

Now let us consider the energy momentum tensor and express it with the flow velocity v^{α} . By using the mean velocity components $\bar{u}^{\alpha}$ it can be written as follows.

$$T^{\alpha\beta} = m_0 c^2 n \bar{u}^{\alpha} \bar{u}^{\beta} + \int f m_0 c^2 (u^{\alpha} - \bar{u}^{\alpha}) (u^{\beta} - \bar{u}^{\beta}) dU. \quad (3 \cdot 22)$$

The integral in the right-hand side is to be calculated after f is determined by solving the Boltzmann equation. The exact solution of it is almost impossible unless the force is absent. In the ordinary hydrodynamical case, where the treatment is not relativistic and the electromagnetic force does not appear, the zero approximation for f , which is the Maxwell distribution function, yields the ordinary hydrodynamical equation for the frictionless fluid as the equation of the mean motion. The first approximation for f yields the Navier-Stokes equation, and the second approximation brings Burnett's equation.⁷⁾ Also in the case of relativistic magnetohydrodynamics, it is desirable to develop a similar method, which is called the Enskog-Chapman method. But as this is too complicated, we will now use the approximate assumptions following Eckart.¹⁾

The zero approximation is

$$T_{(0)}^{\alpha\beta} = w v^{\alpha} v^{\beta} + p \sigma^{\alpha\beta}, \quad (3 \cdot 23)$$

where

$$w = n m_0 c^2 (-\bar{u}^{\alpha} \bar{u}_{\alpha}) = n m_0 c^2 (1 + \overline{u'^{\alpha} u_{\alpha}'}), \quad (3 \cdot 24)$$

is the energy density in a system at rest with respect to an element of the fluid, with the internal energy per unit proper volume $n m_0 c^2 \overline{u'^{\alpha} u_{\alpha}'}$, and

$$\sigma^{\alpha\beta} = g^{\alpha\beta} + v^{\alpha} v^{\beta} \quad (3 \cdot 25)$$

is the tensor indicating the proper space direction of the mean flow. This satisfies the relation

$$T_{\alpha}^{\alpha} = -w + 3p \quad (3 \cdot 26)$$

and its alternative form

$$T_{(0)}^{\alpha\beta} = (w + p) v^{\alpha} v^{\beta} + p g^{\alpha\beta} \quad (3 \cdot 27)$$

is the well-known classical expression for the relativistic fluid without friction.

Next, as the first approximation for $T^{\alpha\beta}$, we will take

$$T_{(1)}^{\alpha\beta} = T_{(0)}^{\alpha\beta} + \mu S_{(1)}^{\alpha\beta}, \quad (3 \cdot 28)$$

where μ is the coefficient of viscosity and $\mu S_{(1)}^{\alpha\beta}$ is the viscous stress tensor defined¹⁾ by

$$S_{(1)}^{\alpha\beta} = \sigma^{\alpha\tau} \sigma^{\beta\delta} (\partial v_\tau / \partial x^\delta + \partial v_\delta / \partial x^\tau) - \frac{2}{3} \sigma^{\alpha\beta} \sigma^{\tau\delta} \cdot \partial v_\tau / \partial x^\delta, \quad (3.29)$$

which satisfies the conditions

$$v_\alpha S_{(1)}^{\alpha\beta} = 0, \quad (3.30)$$

$$S_{(1)\alpha}^\alpha = 0. \quad (3.31)$$

The condition (3.30) means that the viscous tensor is in the direction orthogonal to the flow velocity. The latter condition (3.31) means that the relation (3.26) holds also for the first approximation or that the invariant static pressure is already taken into account in $T_{(0)}^{\alpha\beta}$.

In the non-relativistic approximation $\sigma^{\alpha\beta}$ is reduced as

$$\sigma^{4i} \rightarrow 0, \quad \sigma^{ij} \rightarrow \delta^{ij}, \quad (3.32)$$

so that the viscous tensor becomes the well-known Stokes' form

$$\mu S_{(1)}^{ij} \rightarrow \mu (\partial v^i / \partial x_j + \partial v^j / \partial x_i) - \frac{2}{3} \mu \delta^{ij} \cdot \partial v^k / \partial x^k. \quad (3.33)$$

Lastly adding the equation of state to these equations we have a system of basic equations of flow.

§ 4. Equations for the fully ionized fluid

The fully ionized fluid is composed of ions and electrons. We consider the simplest case where the ions are of only one sort. Moreover we treat here the ideal case involving only the elastic collisions and assume that inelastic processes such as excitations, ionizations, recombinations and nuclear reactions do not occur. We use suffices (i) and (e) to denote quantities for ions and electrons respectively.

In the assumed case both ion and electron rest masses are collision invariants, so that the continuity equations hold for ions and electrons independently.

$$\partial (\rho_{(i)} v_{(i)}^\alpha) / \partial x^\alpha = 0, \quad (4.1)$$

$$\partial (\rho_{(e)} v_{(e)}^\alpha) / \partial x^\alpha = 0. \quad (4.2)$$

The flow equations for ions and electrons can be derived in the same way as in § 3.

$$\partial T_{(i)}^{\alpha\beta} / \partial x^\alpha = j_{(i)\tau} F^{\beta\tau} + \Delta P_{(i)}^\beta, \quad (4.3)$$

$$\partial T_{(e)}^{\alpha\beta} / \partial x^\alpha = j_{(e)\tau} F^{\beta\tau} + \Delta P_{(e)}^\beta, \quad (4.4)$$

where

$$j_{(i)}^\alpha = \int f e_{(i)} u_{(i)}^\alpha dU_{(i)} = e_{(i)} m_{(i)0}^{-1} \rho_{(i)} v_{(i)}^\alpha \quad (4.5)$$

$$j_{(e)}^\alpha = - \int f e u_{(e)}^\alpha dU_{(e)} = -e m_{(e)0}^{-1} \rho_{(e)} v_{(e)}^\alpha \quad (4.6)$$

are the four-currents of ions and electrons and

$$\Delta P_{(i)}^{\beta} = \int m_{(i)0} u_{(i)}^{\beta} \mathcal{A}_{\text{col}} f_{(i)} dU_{(i)} = c^{-1} \int m_{(i)0} u_{(i)}^{\beta} \mathcal{A}'_{\text{col}} f_{(i)}^* d^3 u \quad (4.7)$$

$$\Delta P_{(e)}^{\beta} = \int m_{(e)0} u_{(e)}^{\beta} \mathcal{A}_{\text{col}} f_{(e)} dU_{(e)} = c^{-1} \int m_{(e)0} u_{(e)}^{\beta} \mathcal{A}'_{\text{col}} f_{(e)}^* d^3 u \quad (4.8)$$

are the total changes of four-momenta of ions and electrons by collisions, respectively. Since a collision between identical particles does not change the resultant momentum of particles, only collisions with other particles yield net momentum changes. Hence only a part of $\Delta P_{(i)}^{\alpha}$ gained by the collision with electrons, say $\Delta P_{(ie)}^{\alpha}$, will survive, and also a part of $\Delta P_{(e)}^{\alpha}$ gained by the collision with ions, $\Delta P_{(ei)}^{\alpha}$, will survive.

If we have two relations among $\Delta P_{(i)}^{\alpha}$, $\Delta P_{(e)}^{\alpha}$ and flow variables, we can rewrite the flow equations (4.3) and (4.4) in different forms without $\Delta P_{(i)}^{\beta}$, $\Delta P_{(e)}^{\beta}$, after elimination of them. By the conservation law of the total energy and momentum, the relation

$$\Delta P_{(ie)}^{\alpha} = -\Delta P_{(ei)}^{\alpha}, \quad (4.9)$$

or equivalently

$$\Delta P_{(i)}^{\alpha} = -\Delta P_{(e)}^{\alpha}, \quad (4.10)$$

holds. This is an exact relation, arising from the conservation law of dynamics, but as the second relation we must set a somewhat approximate assumption. Since the velocity change of one of two colliding particles is proportional to the velocity difference between the two particles, we assume

$$\Delta P_{(ei)}^{\alpha} = c_{ei} \eta_{\beta}^{\alpha} (v_{(e)}^{\beta} - v_{(i)}^{\beta}), \quad c_{ei} = |e e_{(i)} \rho_{(e)} \rho_{(i)} m_{(e)0}^{-1} m_{(i)0}^{-1}| \quad (4.11)$$

where η_{β}^{α} may depend on several conditions such as field strength and temperature but to a first approximation it may be taken as a constant η_{β}^{α} . Since in the non-relativistic stationary case the resultant equation reduces to Ohm's law with η as the electric resistivity, η can be interpreted as an extension of electric resistivity.

Now using the two relations (4.10) and (4.11), we can eliminate $\Delta P_{(i)}^{\beta}$ and $\Delta P_{(e)}^{\beta}$ and obtain the equations of flow

$$\frac{\partial (T_{(i)}^{\alpha\beta} + T_{(e)}^{\alpha\beta})}{\partial x^{\alpha}} = (j_{(i)\gamma} + j_{(e)\gamma}) F^{\beta\gamma}, \quad (4.12)$$

$$\frac{\partial (m_{(e)0} T_{(i)}^{\alpha\beta} - m_{(i)0} T_{(e)}^{\alpha\beta})}{\partial x^{\alpha}} = (m_{(e)0} j_{(i)\gamma} - m_{(i)0} j_{(e)\gamma}) F^{\beta\gamma} + (m_{(e)0} + m_{(i)0}) c_{ei} \eta_{\alpha}^{\beta} (v_{(i)}^{\alpha} - v_{(e)}^{\alpha}). \quad (4.13)$$

Thus we have obtained the basic equations for fully ionized fluid in terms of ion and electron variables. In order to describe such a composed plasma as if it were a single unified fluid we must introduce total flow variables describing the plasma flow as a whole,

$$\text{total mass density: } \rho = \rho_{(i)} + \rho_{(e)}, \quad (4.14a)$$

$$\text{total mass velocity: } v^{\alpha} = \rho^{-1} (\rho_{(i)} v_{(i)}^{\alpha} + \rho_{(e)} v_{(e)}^{\alpha}), \quad (4.14b)$$

$$\text{total charge density: } \sigma = e_{(i)} m_{(i)0}^{-1} \rho_{(i)} - e m_{(e)0}^{-1} \rho_{(e)}, \quad (4.14c)$$

$$\text{total current density: } j^\alpha = e_{(i)} m_{(i)0}^{-1} \rho_{(i)} v_{(i)}^\alpha - e m_{(e)0}^{-1} \rho_{(e)} v_{(e)}^\alpha. \quad (4.14d)$$

Inversely the ion and the electron variables can be written with the total flow variables

$$\rho_{(i)} = (e\rho + m_{(e)}\sigma) / (e + m_{(e)} m_{(i)}^{-1} e_{(i)}), \quad (4.15a)$$

$$\rho_{(e)} = (e_{(i)}\rho - m_{(i)}\sigma) / (e_{(i)} + m_{(i)} m_{(e)}^{-1} e), \quad (4.15b)$$

$$v_{(i)}^\alpha = (e\rho v^\alpha + m_{(e)} j^\alpha) / (e\rho + m_{(e)}\sigma) \quad (j_{(i)}^\alpha = e_{(i)} m_{(i)0}^{-1} \rho_{(i)} v_{(i)}^\alpha), \quad (4.15c)$$

$$v_{(e)}^\alpha = (e_{(i)}\rho v^\alpha m_{(e)} j^\alpha) / (e_{(i)}\rho - m_{(i)}\sigma) \quad (j_{(e)}^\alpha = -e m_{(e)0}^{-1} \rho_{(e)} v_{(e)}^\alpha). \quad (4.15d)$$

It is not difficult to write the basic equations, (4.1), (4.2), (4.12) and (4.13) in terms of new variables ρ , σ , v^α and j^α by performing the variable transformations (4.15). But the resultant equations are not so simple in general, and this seems to show that it is neither natural nor advantageous to describe two general interacting, non-linear, relativistic flows as a unified flow. Such a picture of the total flow seems to be successful in the case of a slow or moderate speed plasma.

However we will give here the equations of total flow for the most important case of a neutral frictionless plasma of ions and electrons with $e_{(i)} = +e$, $e_{(e)} = -e$, $m_{i(0)} \gg m_{(e)0}$, $\sigma = 0$. In this case (4.15) reduces to

$$\rho_{(i)} = \rho, \quad \rho_{(e)} = m_{(e)0} m_{(i)0}^{-1} \rho, \quad (4.16a)$$

$$v_{(i)}^\alpha = v^\alpha + m_{(e)0} j^\alpha / e\rho, \quad (4.16b)$$

$$v_{(e)}^\alpha = -v^\alpha + m_{(i)0} j^\alpha / e\rho. \quad (4.16c)$$

Since

$$\rho_{(i)} v_{(i)}^\alpha = \rho v^\alpha + m_{(e)} e^{-1} j^\alpha$$

$$\rho_{(e)} v_{(e)}^\alpha = -m_{(e)} m_{(i)}^{-1} \rho v^\alpha + m_{(e)} e^{-1} j^\alpha$$

the equations of continuity, (4.1) and (4.2), become

$$\partial(e\rho v^\alpha + m_{(e)} j^\alpha) / \partial x^\alpha = 0$$

$$\partial(-e\rho v^\alpha + m_{(i)} j^\alpha) / \partial x^\alpha = 0.$$

or equivalently

$$\partial j^\alpha / \partial x^\alpha = 0 \quad (4.17)$$

$$\partial(\rho v^\alpha) / \partial x^\alpha = 0. \quad (4.18)$$

These are the conservation equations of charge- and mass-flows.

Since

$$v_{(i)}^\alpha v_{(i)}^\beta = v^\alpha v^\beta + (j^\alpha v^\beta + j^\beta v^\alpha) m_{(e)0} / e\rho + j^\alpha j^\beta (m_{(e)0} / e\rho)^2$$

$$v_{(e)}^\alpha v_{(e)}^\beta = v^\alpha v^\beta - (j^\alpha v^\beta + j^\beta v^\alpha) m_{(i)0} / e\rho + j^\alpha j^\beta (m_{(i)0} / e\rho)^2$$

$$j_{(i)}^\alpha + j_{(e)}^\alpha = j^\alpha,$$

the first equation of flow, (4.12), becomes

$$\partial T^{\alpha\beta}/\partial x^\alpha = j_\tau F^{\beta\tau}, \quad (4.19)$$

where

$$T^{\alpha\beta} = A v^\alpha v^\beta + B (j^\alpha v^\beta + j^\beta v^\alpha) + C j^\alpha j^\beta + p g^{\alpha\beta} \quad (4.20)$$

with

$$A = W_{(i)} + W_{(e)}, \quad B = (m_{(e)0} W_{(i)} - m_{(i)0} W_{(e)}) / e\rho, \quad C = (m_{(e)0}^2 W_{(i)} + m_{(i)0}^2 W_{(e)}) / (e\rho)^2 \\ W_{(i)} = w_{(i)} + p_{(i)}, \quad W_{(e)} = w_{(e)} + p_{(e)}, \quad p = p_{(i)} + p_{(e)}. \quad (4.21)$$

Since

$$m_{(e)0} j_{(i)}^\alpha - m_{(i)0} j_{(e)}^\alpha = e\rho v^\alpha + m_{(i)} j^\alpha, \\ (m_{(e)0} + m_{(i)0}) c_{ei} \eta (v_{(i)}^\alpha - v_{(e)}^\alpha) = \rho \eta j^\alpha,$$

the second equation of flow (4.13) becomes

$$\partial R^{\alpha\tau}/\partial x^\alpha = (e\rho v_\tau + m_{(i)0} j_\tau) F^{\beta\tau} + e\rho \eta j^\beta, \quad (4.22)$$

where

$$R^{\alpha\beta} = B e \rho v^\alpha v^\beta + C e \rho (j^\alpha v^\beta + j^\beta v^\alpha) + j^\alpha j^\beta (m_{(e)0}^2 W_{(i)} - m_{(i)0}^2 W_{(e)}) / (e\rho)^3 \\ + (m_{(e)0} p_{(i)} - m_{(i)0} p_{(e)}) g^{\alpha\beta}. \quad (4.23)$$

Thus we have obtained basic equations (4.17), (4.18), (4.19) and (4.22) for the total flow, but this is not necessarily convenient, but sometimes it is preferable to use (4.3) and (4.4) with (4.11) or to use (4.19) and one of (4.3) and (4.4). Of course, to complete the system of basic equations we must add the equation of state.

§ 5. Equations for the partially ionized fluid

The partially ionized fluid is composed of neutral atoms, positive ions and negative electrons. We consider the simple case where both atoms and ions are of only one sort and there occurs only elastic collisions. We use the suffices (a), (i), (e) to denote the quantities for atoms, ions and electrons, respectively.

Equations for such a plasma can be obtained in a similar way to that used in § 4. The continuity equations for the mass flow hold for atoms, ions and electrons independently:

$$\partial (\rho_{(a)} v_{(a)}^\alpha) / \partial x^\alpha = 0, \quad (5.1)$$

$$\partial (\rho_{(i)} v_{(i)}^\alpha) / \partial x^\alpha = 0, \quad (5.2)$$

$$\partial (\rho_{(e)} v_{(e)}^\alpha) / \partial x^\alpha = 0. \quad (5.3)$$

The flow equations for atoms, ions and electrons can be derived in the same way as in § 3 and § 4.

$$\partial T_{(a)}^{\alpha\beta}/\partial x^\alpha = \Delta P_{(ai)}^\beta + \Delta P_{(ae)}^\beta, \quad (5.4)$$

$$\partial T_{(i)}^{\alpha\beta}/\partial x^\alpha = j_{(i)\gamma} F^{\beta\gamma} + \Delta P_{(ia)}^\beta + \Delta P_{(ie)}^\beta, \quad (5.5)$$

$$\partial T_{(e)}^{\alpha\beta}/\partial x^\alpha = j_{(e)\gamma} F^{\beta\gamma} + \Delta P_{(ea)}^\beta + \Delta P_{(ei)}^\beta, \quad (5.6)$$

where for instance $\Delta P_{(ai)}$ is the net momentum change of atoms gained by the collision with ions, and the other quantities have similar meanings. The relations similar to (4.9) are

$$\Delta P_{(ai)}^\alpha = -\Delta P_{(ia)}^\alpha, \quad \Delta P_{(ae)}^\alpha = -\Delta P_{(ea)}^\alpha, \quad \Delta P_{(ie)}^\alpha = -\Delta P_{(ei)}^\alpha. \quad (5.7)$$

As the relations similar to (4.11) we assume

$$\Delta P_{(ei)}^\alpha = c_{ei} \eta_\beta^\alpha (v_{(e)}^\beta - v_{(i)}^\beta), \quad (5.8a)$$

$$\Delta P_{(ea)}^\alpha = c_{ea} \eta_\beta'^\alpha (v_{(e)}^\beta - v_{(a)}^\beta), \quad c_{ea} = e^2 \rho_{(e)} \rho_{(a)} m_{(e)0}^{-1} m_{(a)0}^{-1}, \quad (5.8b)$$

$$\Delta P_{(ia)}^\alpha = c_{ia} \eta_\beta''^\alpha (v_{(i)}^\beta - v_{(a)}^\beta), \quad c_{ia} = e_{(i)}^2 \rho_{(i)} \rho_{(a)} m_{(i)0}^{-1} m_{(a)0}^{-1}. \quad (5.8c)$$

The terms η_β^α , $\eta_\beta'^\alpha$, $\eta_\beta''^\alpha$ have meanings of particle resistivity, being proportional to the reciprocal collision time intervals, and to a first approximation they may be constants

$$\eta_\beta^\alpha = \eta g_\beta^\alpha, \quad \eta_\beta'^\alpha = \eta' g_\beta^\alpha, \quad \eta_\beta''^\alpha = \eta'' g_\beta^\alpha. \quad (5.9)$$

Adding three equations, (5.4), (5.5) and (5.6), we have

$$\partial (T_{(a)}^{\alpha\beta} + T_{(i)}^{\alpha\beta} + T_{(e)}^{\alpha\beta}) / \partial x^\alpha = (j_{(i)\gamma} + j_{(e)\gamma}) F^{\beta\gamma}. \quad (5.10)$$

This is the most convenient equation to describe the plasma flow as a whole. As the basic equations of flow we can take (5.10) and two of (5.4), (5.5) and (5.6) with (5.8) and (5.9). Such three equations of flow and the continuity equations, (5.1), (5.2) and (5.3), are the basic equations for the partially ionized fluid. Of course for the complete system of the basic equations we must add the equation of state.

In order to obtain the picture of a single unified fluid, we can introduce the total flow variables ρ , σ , v^α and j^α in the same way as in §4, but the number of new variables is not sufficient to eliminate atom, ion and electron variables $\rho_{(a)}$, $v_{(a)}^\alpha$, $\rho_{(i)}$, $v_{(i)}^\alpha$, $\rho_{(e)}$ and $v_{(e)}^\alpha$. This shows that the general partially ionized plasma should be treated as a composed medium and not as a simple unified fluid.

§ 6. Generalized circulation and vortex theorems for isentropic flows of simple perfect fluids

Basic equations for a simple fluid of a perfect gas with charge e are the equation of continuity

$$\partial(\rho v^\alpha) / \partial x^\alpha = 0, \quad (6.1)$$

the equation of motion

$$\partial(\rho J v^\alpha v^\beta + p g^{\alpha\beta}) / \partial x^\alpha = e m_0^{-1} \rho v_\gamma F^{\alpha\gamma}, \quad (6.2)$$

the equation of the relativistic thermodynamics

$$T dS = dJ - \rho^{-1} dp \quad (6.3)$$

and the equation of state, which we assume to be barotropic, where

$$J = (w + p) / \rho \quad (6.4)$$

and T is the temperature, S the entropy and J the heat content per unit rest mass.

In order to derive the conservation theorems of generalized circulation and vorticity, we shall rearrange the basic equations. By using (6.1) we can write (6.2) in the form

$$v^\alpha \frac{\partial}{\partial x^\alpha} (J v^\beta) = -\frac{1}{\rho} \frac{\partial p}{\partial x_\beta} + \frac{e}{m_0} v_\tau F^{\beta\tau}. \quad (6.5)$$

Further by means of (6.3) this becomes

$$v_\alpha \frac{\partial}{\partial x_\alpha} (J v^\beta) = \left(T \frac{\partial S}{\partial x_\beta} - \frac{\partial J}{\partial x_\beta} \right) + \frac{e}{m_0} v_\alpha F^{\beta\alpha}. \quad (6.6)$$

By differentiating (3.12) we can show

$$v_\alpha \frac{\partial}{\partial x_\beta} (J v^\alpha) = -\frac{\partial J}{\partial x_\beta}. \quad (6.7)$$

From (6.6) and (6.7) we have

$$v_\alpha \left\{ \frac{\partial}{\partial x_\alpha} (J v^\beta) - \frac{\partial}{\partial x_\beta} (J v^\alpha) \right\} = T \frac{\partial S}{\partial x^\beta} + \frac{e}{m_0} v_\alpha F^{\beta\alpha} \quad (6.8)$$

or

$$v_\alpha \left\{ \frac{\partial}{\partial x_\alpha} \left(J v^\beta + \frac{e}{m_0} A^\beta \right) - \frac{\partial}{\partial x_\beta} \left(J v^\alpha + \frac{e}{m_0} A^\alpha \right) \right\} = J \frac{\partial S}{\partial x^\beta}. \quad (6.9)$$

This is the generalization of the vorticity equations of classical hydrodynamics.

Now let us consider an isentropic flow. For such a flow (6.6) reduces to

$$v_\alpha \frac{\partial}{\partial x_\alpha} \left(J v^\beta + \frac{e}{m_0} A^\beta \right) = -\frac{\partial J}{\partial x_\beta} + \frac{e}{m_0} v_\alpha \frac{\partial A^\beta}{\partial x_\beta}. \quad (6.10)$$

When a closed curve C , whose line element is ∂x^α , is given in the four dimensional world, we define the generalized circulation I' with respect to a curve C

$$I' = \int_C (J v_\alpha + e m_0^{-1} A_\alpha) \partial x^\alpha. \quad (6.11)$$

Then the variation of I' becomes

$$\begin{aligned} \frac{dI'}{d\tau} &= \int_C \left[\frac{d}{d\tau} (J v_\alpha + e m_0^{-1} A_\alpha) \partial x^\alpha + (J v_\alpha + e m_0^{-1} A_\alpha) \frac{d \partial x^\alpha}{d\tau} \right] \\ &= \int_C \left[\left(-\frac{\partial J}{\partial x_\alpha} + e m_0^{-1} v_\beta \frac{\partial A^\beta}{\partial x^\alpha} \right) \partial x^\alpha + (J v_\alpha + e m_0^{-1} A_\alpha) \partial v^\alpha \right] \\ &= \int_C \left[-\delta J + \frac{1}{2} J \delta (v_\alpha v^\alpha) + e m_0^{-1} v_\beta \delta A^\beta + e m_0^{-1} A_\alpha \delta v^\alpha \right] \end{aligned}$$

$$\begin{aligned}
 &= \int_C \partial [-J + em_0^{-1} A_\alpha v^\alpha] \\
 &= 0.
 \end{aligned} \tag{6.12}$$

Thus we have generalized Kelvin's theorem of circulation of classical hydrodynamics in the case of relativistic magnetohydrodynamics. It should be noticed that in our case the constant in the theorem is not a formal four-dimensional generalization of the expression of classical hydrodynamics, but the integral (6.11) remains constant with respect to an arbitrary closed curve in the Minkowski space time.

From the above obtained theorem we can derive the theorem of vorticity in the usual way. By the generalized Stokes' integral theorem in the relativity theory,⁸⁾ the integral (6.11) can be written as a surface integral over the surface S enclosed by a given closed curve C

$$\Gamma = \iint_S w^{\alpha\beta} \partial S_{\alpha\beta}, \tag{6.13}$$

where

$$w^{\alpha\beta} = \frac{\partial}{\partial x_\alpha} (J v^\beta + em_0^{-1} A^\beta) - \frac{\partial}{\partial x_\beta} (J v^\alpha + em_0^{-1} A^\alpha) \tag{6.14}$$

and $\partial S_{\alpha\beta}$ is the surface element. If we write the invariant form in the integral symbol as

$$w^{\alpha\beta} \partial S_{\alpha\beta} = w_n \partial S, \quad (\partial S)^2 = \partial S_{\alpha\beta} \cdot \partial S^{\alpha\beta}$$

it becomes the familiar form

$$\Gamma = \iint_S w_n \partial S. \tag{6.15}$$

Thus the circulation theorem (6.12) can be converted into the form of Helmholtz's theorem of vortex, namely the strength of generalized vorticity $w_n \partial S$ remains invariant during the motion of the fluid and the generalized vorticity can be neither created nor destroyed. This is the generalization of the classical vorticity theorem. It should be noticed that the generalized vorticity in the theorem is not a formal four-dimensional generalization of the expression of classical hydrodynamics, but we must generalize it in the form (6.14). This shows, inversely, that the formal generalization

$$\left(\frac{\partial v^\beta}{\partial x_\alpha} - \frac{\partial v^\alpha}{\partial x_\beta} \right) \partial S_{\alpha\beta}$$

does not remain invariant and can be created and destroyed even in the field free case $A^\alpha = 0$.

§ 7. General shock conditions for one dimensional flow of a simple fluid in a uniform electromagnetic field

Since, as is well known, the energy momentum tensor of the electromagnetic field

$$T_{\text{field}}^{\alpha\beta} = F_{\gamma}^{\alpha} F^{\gamma\beta} + \frac{1}{2} g^{\alpha\beta} F_{\gamma\delta} F^{\gamma\delta} \quad (7.1)$$

satisfies

$$\partial T_{\text{field}}^{\alpha\beta} / \partial x^{\beta} = -j_{\gamma} F^{\alpha\gamma}, \quad (7.2)$$

the flow equation of a simple fluid can be written as

$$\partial (T_{\text{flow}}^{\alpha\beta} + T_{\text{field}}^{\alpha\beta}) / \partial x^{\beta} = 0, \quad (7.3)$$

where

$$T_{\text{flow}}^{\alpha\beta} = (\varpi + p) v^{\alpha} v^{\beta} + p g^{\alpha\beta}, \quad (7.4)$$

neglecting the viscous terms.

Let us consider a one dimensional flow in a uniform electromagnetic field. We assume that the fluid flows in x_1 direction ($v_1 \neq 0$, $v_2 = v_3 = 0$), the external field is constant and a shock wave, whose front is in the plane perpendicular to the x_1 axis, is travelling in x_1 direction with a uniform velocity U . Now let us transform the coordinate system so as to be at rest relative to the shock front and denote the quantities referred to this system with prime. Since the shock front is at rest in the system, its position is a point x'_0 , and if we denote quantities ahead of the shock by a suffix (1) and those behind the shock by (2), the fluid is flowing with a velocity $v'_{(1)}$ into the shock and then into the back region of the shock with a velocity $v'_{(2)}$. As all the quantities depend only on x'_1 , the equation (7.3) reduces to

$$\partial (T'^{\alpha 1}_{\text{flow}} + T'^{\alpha 1}_{\text{field}}) / \partial x'_1 = 0. \quad (7.5)$$

Though it is usual to assume, neglecting the viscous terms, that at the shock front discontinuities of fluid parameters occur, we can show that this is only an approximation to a complicated continuous flow when the viscosity is taken into account. Thus the equation (7.5) should hold across the shock front approximately and we have

$$T'^{\alpha 1}_{\text{flow}} + T'^{\alpha 1}_{\text{field}} = \text{const. in flow.} \quad (7.6)$$

or

$$(\varpi_{(1)} + p_{(1)}) (v'_{(1)})^2 + p'_{(1)} + T'^{11}_{\text{field}(1)} = (\varpi_{(2)} + p_{(2)}) (v'_{(2)})^2 + p'_{(2)} + T'^{11}_{\text{field}(2)}, \quad (7.7)$$

$$(\varpi_{(1)} + p_{(1)}) v'_{(1)} v'^4_{(1)} + T'^{14}_{\text{field}(1)} = (\varpi_{(2)} + p_{(2)}) v'_{(2)} v'^4_{(2)} + T'^{14}_{\text{field}(2)}. \quad (7.8)$$

This is a generalization of Rankine-Hugoniot's relations.

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On the Orbital Approach to the Many-Electron Problem in Molecule

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The lowest ${}^3\Sigma_u^+$ and ${}^1\Sigma_u^+$ states of the hydrogen molecule, the interaction energy between two normal helium atoms and the ${}^3B_{1u}$ and ${}^1B_{1u}$ states of the ethylene molecule are treated by the method of the molecular orbitals in the single configuration approximation. The results are encouraging and the reason for this success is that we have used molecular orbitals which are a little more flexible than the conventional LCAO MO's. It is confirmed that the failure of the conventional ASMO LCAO approximation does not necessarily imply the break-down of the useful concept of "molecular orbital" itself.

§ 1. Introduction

It is convenient if we can describe effectively an electronic state of a molecule by one single electronic configuration. In this approximation each electron has its own orbital and the physical picture is simple and appeals to our naive imagination. This approximate concept has worked well in qualitative discussions but, if we try to put the discussions on more quantitative bases by specifying the forms of the orbitals in conventional manner, we often find rather discouraging results. In recent years several authors have stressed the necessity of discarding this attractive concept of the single electronic configuration. Coulson et al.¹⁾ stressed the significance of the so-called configuration interaction and the accompanied difficulties of calculation. In their paper we find, for instance, the following sentence: "Thus neither the description of a state by one single configuration wave function, nor of a spectral transition as a one-electron phenomenon, is sufficiently close to the physical facts to give a satisfactory working picture". Moffitt's attitude²⁾ is more radical in discrediting the conventional method of ASMO LCAO with CI and proposing a new prescription of calculation, the method of atoms in molecules. Coulson et al. are absolutely right in remarking that, as far as we use the conventional ASMO LCAO method, we should proceed beyond the single configuration approximation by superposing necessary number of configurations. Also, as far as we are not able to get satisfactory numerical results from the conventional non-empirical method within reasonable labor, we should estimate properly the merits of the method of atoms in molecules and other related semi-empirical methods. Here is, however, the problem of the physical interpretation. It appears that the concept of the single configuration has been faded unreasonably by these and other influential authors. This reminds us of the history of the development of the theory of nucleus. In the earlier stage, the people attempted to proceed with the independent particle model but in the meanwhile there appeared the influential

work of N. Bohr in 1936, which provided the thereafter prevailing picture of the nucleon correlation in the nucleus. In 1949, however, G. Mayer and others succeeded to restore the honour of the independent particle model in a remarkable manner and older physical pictures of the nucleus had to be reexamined from the new standpoint. Of course, the correlation of nucleons inside nuclei may have several distinct features from that of electrons in molecules and the analogy here mentioned might not be suitable one. But if we can show, in the many-electron problem of molecules, that the orbital approach reveals far reaching validity than usually conceived, it is of interest by itself and a new light might be thrown on the physical interpretation *à la* Moffitt of electron correlation in molecules.

The following three sections are devoted to the description of calculations on the H_2 molecule (§ 2), the He-He interaction (§ 3) and the ethylene molecule (§ 4), performed within the single configuration approximation. The results are encouraging. It seems that we can expect to obtain good results in many cases by using the molecular orbitals which are a little more flexible than the usual LCAO MO's. In the last section (§ 5) we shall discuss at some length the results of the calculations in the preceding sections.

§ 2. Hydrogen molecule

The $1s\sigma\ 2p\sigma\ ^3\Sigma_u^{+3)}$ and $^1\Sigma_u^{+}$ states of the hydrogen molecule are treated by the method of the molecular orbital within the single configuration approximation. The problem is closely related to that of the $^3\Sigma_u^{-}$ and $^3\Sigma_u^{+}$ states of the oxygen molecule and of the $^3B_{1u}$ and $^1B_{1u}$ states of the ethylene molecule, which were treated successfully by Moffitt's new method, the method of atoms in molecules.

(a) LCAO MO approximation

We begin with the following two molecular orbitals of LCAO type,

$$\varphi_g = N_g(s_a + s_b) ; \sigma_g, \quad (1)$$

$$\varphi_u = N_u(s_a' - s_b') ; \sigma_u. \quad (2)$$

Here N_g and N_u are the normalization constants and

$$s_a = (Z^3/\pi)^{1/2} \exp(-Zr_a), \quad s_b = (Z^3/\pi)^{1/2} \exp(-Zr_b), \\ s_a' = (Z'^3/\pi)^{1/2} \exp(-Z'r_a), \quad s_b' = (Z'^3/\pi)^{1/2} \exp(-Z'r_b).$$

Then the wave functions for the lowest $^3\Sigma_u^{+3)}$ and $^1\Sigma_u^{+}$ states of the hydrogen molecule are, omitting the spin parts,

$$\Psi(^3\Sigma_u^{+3)}) = (1/\sqrt{2}) \{ \varphi_g(1)\varphi_u(2) - \varphi_u(1)\varphi_g(2) \}, \quad (3)$$

$$\Psi(^1\Sigma_u^{+}) = (1/\sqrt{2}) \{ \varphi_g(1)\varphi_u(2) + \varphi_u(1)\varphi_g(2) \}. \quad (4)$$

The Hamiltonian of the system is (in the atomic units)

$$H(1, 2) = \left(-\frac{1}{2} \Delta_1 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} \right) + \left(-\frac{1}{2} \Delta_2 - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} \right) + \frac{1}{r_{12}}. \quad (5)$$

This expression includes electronic terms only. The orbital approach is exact if we neglect the last term, $1/r_{12}$, the repulsive interaction between two electrons. The expressions for the electronic energies are

$$E_e(^3\Sigma_u^+) = H_g + H_u + J_{gu} - K_{gu}, \quad (6)$$

$$E_e(^1\Sigma_u^+) = H_g + H_u + J_{gu} + K_{gu}, \quad (7)$$

where

$$H_g = \int \varphi_g \left(-\frac{1}{2} \Delta - \frac{1}{r_a} - \frac{1}{r_b} \right) \varphi_g d\tau, \quad (8)$$

$$H_u = \int \varphi_u \left(-\frac{1}{2} \Delta - \frac{1}{r_a} - \frac{1}{r_b} \right) \varphi_u d\tau, \quad (9)$$

$$J_{gu} = \iint \varphi_g(1) \varphi_g(1) (1/r_{12}) \varphi_u(2) \varphi_u(2) d\tau_1 d\tau_2, \quad (10)$$

$$K_{gu} = \iint \varphi_g(1) \varphi_u(1) (1/r_{12}) \varphi_g(2) \varphi_u(2) d\tau_1 d\tau_2. \quad (11)$$

In this case the singlet-triplet separation is given as below,

$$\Delta = E_e(^1\Sigma_u^+) - E_e(^3\Sigma_u^+) = 2K_{gu}. \quad (12)$$

Since the ground state of the hydrogen molecule is of the symmetry of $^1\Sigma_g^+$ and we are concerned with the lowest $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states we can calculate the energies of these two states by straightforward application of the variation method. The parameters are Z and Z' . It is expected that we should take $Z > 1$ and $Z' < 1$. Coulson and Fischer⁽¹⁾ chose the value of $Z=1$ as a compromise between these two requirements. We examine here three cases, $Z=Z'=1$, $Z=Z' \neq 1$ and $Z \neq Z'$.

$$(a-1) \quad Z=Z'=1.$$

In the case of $Z=Z'$ the expressions of the wave functions, (3) and (4), can be recast in the following familiar forms:

$$\Psi(^3\Sigma_u^+) \sim s_a(1)s_b(2) - s_b(1)s_a(2), \quad (13)$$

$$\Psi(^1\Sigma_u^+) \sim s_a(1)s_a(2) - s_b(1)s_b(2). \quad (14)$$

These expressions are usually interpreted in such a way that the $^3\Sigma_u^+$ state reduces to two normal H atoms and the $^1\Sigma_u^+$ state to H^+ and H^- at the infinite separation. The correspondences to the case of the $^3\Sigma_u^+$ and $^3\Sigma_u^-$ states of the oxygen molecule and also to the case of the $^3B_{1u}$ and $^1B_{1u}$ states of the ethylene molecule become evident now. However, this interpretation loses its apparent meaning in the case of $Z \neq Z'$ and for the purpose of the present paper the original molecular orbital expressions, (3) and (4), are preferable.

The calculations are performed at three values of the internuclear distance R , 1.0, 1.5 and 2.0 au, special attention being placed on the case of $R=2$. Table 1 contains

the results of the calculations in the case of $Z=Z'=1$. It seems convenient to show the values of the repulsive energy for the ${}^3\Sigma_u^+$ state, which is given by the formula, $E_e({}^3\Sigma_u^+) + (1/R) - (-1)$, where $(1/R)$ is the Coulomb repulsive energy between two nuclei and (-1) means the sum of the energies of two hydrogen atoms in the ground $1s$ -state. The atomic units* are used throughout this paper, unless the contrary is explicitly stated. The calculated repulsive energies of the state in Kcal mole are found in Table 2. The values of the case of $Z=Z'=1$ are listed in the column (a-1) and if we compare these with the results of the accurate calculation of James, Coolidge and Present,⁽⁴⁾ listed in the last column (JCP), we find that the assumption of $Z=Z'=1$ yields very unsatisfactory numerical results. In Present's calculation on the ${}^1\Sigma_u^+$ state,⁽⁵⁾ the attention is focused mainly on the internuclear distance around $R=2.4$ au and unfortunately it seems that we have no standard values of the energy of the state over the range of $R=1\sim 2$ au, to check the accuracies of our calculations. Nevertheless, a provisional estimation based upon Present's results gives the value shown below for the singlet-triplet separation Δ at $R\cong 2$ au, which seems sufficiently accurate for our present purpose:

$$\Delta \cong 0.14 \text{ au } (R \cong 2 \text{ au}). \quad (15)$$

Accepting this value we see that the accuracy of the calculation under the restricted assumption of $Z=Z'=1$ is even worse for the ${}^1\Sigma_u^+$ state than for the ${}^3\Sigma_u^+$ state, because $\Delta=0.30$ in this case according to Table 1. The separation is grossly exaggerated as is the case for the ${}^3\Sigma_u^+ - {}^3\Sigma_u^-$ separation of the oxygen molecule and for the ${}^3B_{1u} - {}^1B_{1u}$

Table 1. ($Z=Z'=1$)

R	$E_e({}^3\Sigma_u^+)$	$E_e({}^1\Sigma_u^+)$	Δ
1.0	-1.295085	-1.027282	0.267803
1.5	-1.347656	-1.063634	0.284022
2.0	-1.346042	-1.042683	0.303359

Table 2. The repulsive energy of the ${}^3\Sigma_u^+$ state in Kcal mole

R	(a-1)	(a-3)	(b)	(HL)	(JCP)
1.0	442.5	249.9	246.8		245†
1.5	200.2	128.6	126.8	142	119.8
2.0	96.6	71.0	71.0		65.9

(a-1): LCAO MO $Z=Z'=1$

(a-3): LCAO MO $Z \neq Z'$

(b): James MO

(HL): Hirschfelder and Linnett⁽⁵⁾

(JCP): James, Coolidge and Present⁽⁴⁾

† The value from the formula (12) of HL.

* Length: $a_0 = 0.5292 \times 10^{-8}$ cm (Bohr radius).

Energy: $e^2/a_0 = 27.21$ eV = 627.7 Kcal/mole (twice the ionization energy of hydrogen).

separation of the ethylene molecule. To summarize, both the absolute energy values and the relative positions of the lowest ${}^3\Sigma_u^+$ and ${}^1\Sigma_u^+$ states of the hydrogen molecule are given only very inaccurately in this first stage of approximation.

$$(a-2) \quad Z=Z' \neq 1.$$

As the second stage of approximation, let us try to improve the calculation by varying Z , still keeping the restriction of $Z=Z'$. The calculation is performed at $R=2$ only and the results are displayed in Table 3. It is observed that the optimum values

Table 3. ($Z=Z' \neq 1$, $R=2$)

Z	$E_e({}^3\Sigma_u^+)$	$E_e({}^1\Sigma_u^+)$
0.5	-1.09752	-0.963623
0.75	-1.29423	-1.08121
0.875	-1.33590	-1.07921
1.0	-1.34604	-1.04268
1.25	-1.28062	-0.874563

of Z would lie around $0.9 \sim 1.0$ for ${}^3\Sigma_u^+$ and around 0.8 for ${}^1\Sigma_u^+$ but for the present purpose it would be sufficient to select from Table 3 the next set of the energy values as the best combination:

$$\left. \begin{aligned} E_e({}^3\Sigma_u^+) &= -1.34604 \quad (Z=1) \\ E_e({}^1\Sigma_u^+) &= -1.08121 \quad (Z=0.75) \end{aligned} \right\} \quad (16)$$

Then we find $\Delta = E_e({}^1\Sigma_u^+) - E_e({}^3\Sigma_u^+) = 0.26483$. We see that $E_e({}^1\Sigma_u^+)$ is improved by about 1 eV but for $E_e({}^3\Sigma_u^+)$ the older value with $Z=1$ happens to remain nearly the best one under the variation of Z , no improvement being brought about. As a whole the accuracy of calculation is still very poor.

$$(a-3) \quad Z \neq Z'.$$

We should like to stress here that it is our "Leit-motiv" throughout the present work to give the freedoms of separate deformations to the bonding and anti-bonding molecular orbitals. For the LCAO-type molecular orbitals φ_g and φ_u , given in (1) and (2), it is effected by taking Z and Z' as two separately variable parameters. A complete variation treatment concerning these two parameters is desirable, of course, but in the present calculation the values of the parameters are fixed by simple guess work, for convenience. Table 4 exhibits the values of the parameters chosen primarily for the ${}^3\Sigma_u^+$ state³⁾ and later used also for the ${}^1\Sigma_u^+$ state. Notice that each set of Z and Z' obeys the restrictions; $Z > Z'$, $Z+Z'=2$ and $(1/2)(ZR-Z'R)=0.5$. The last restriction permits us to use KAIK table⁸⁾ conveniently. The results of the calculation are shown in Table 5. Comparing this table ($Z \neq Z'$) with Table 1 ($Z=Z'=1$), we confirm again that the calculation with the restriction of $Z=Z'=1$ yields very poor results ($0.1 \text{ au} = 2.721 \text{ eV}$). The repulsive energies of the ${}^3\Sigma_u^+$ state calculated from $E_e({}^3\Sigma_u^+)$ of

Table 4

R	ZR	$Z'R$	2α	2β
1.0	1.5	0.5	1.5	0.5
1.5	2.0	1.0	2.0	1.0
2.2	2.5	1.5	2.5	1.5

Table 5. ($Z \neq Z'$)

R	$E_e(^3\Sigma_u^+)$	$E_e(^1\Sigma_u^+)$	J
1.0	-1.60162	-1.47751	0.12411
1.5	-1.46166	-1.24193	0.21973
2.0	-1.38681	-1.11140	0.27541

Table 5 are listed in the column (a-3) of Table 2. It is seen that we have succeeded to approach rather closely to the values of (JCP), still remaining within the single configuration approximation. (1 Kcal mole = 0.04335 eV) As for the $^1\Sigma_u^+$ state, however, it is highly desirable to improve the calculation further because $J=0.2754$ at $R=2$, while the actual value of the separation energy seems to be $J \approx 0.14$. We have attempted to improve the calculation for $^1\Sigma_u^+$ by choosing the following set of the parameters:

$$ZR=3.0 \text{ and } Z'R=1.0, (R=2).$$

This choice has an aim to reduce the degree of overlapping between the orbitals φ_z and φ_u . The results are

$$E_e(^3\Sigma_u^+) = -1.30218, E_e(^1\Sigma_u^+) = -1.13555, J=0.16663.$$

Summarizing the results obtained hitherto, we find the following values of $E_e(^3\Sigma_u^+)$ and $E_e(^1\Sigma_u^+)$ at $R=2$ as the best combination;

$$\begin{aligned} E_e(^3\Sigma_u^+) &= -1.38681 \quad (Z=1.25, Z'=0.75), \\ E_e(^1\Sigma_u^+) &= -1.13555 \quad (Z=1.5, Z'=0.5). \end{aligned} \quad (17)$$

This set yields the value $J=0.25126$ as the singlet-triplet separation and it simply means that the energy of the $^1\Sigma_u^+$ state here obtained still remains too high. More careful choices of Z and Z' will bring about better results but probably we could not expect much from such a source of refinement.

(b) James-type MO approximation

We use here the following molecular orbitals and tentatively call them James-type molecular orbitals:

$$\varphi_g \sim (1 + c\eta^2) \exp(-\alpha\hat{r}), \quad (18)$$

$$\varphi_u \sim \eta \cdot \exp(-\beta\hat{r}), \quad (19)$$

$$\hat{r} = (r_a + r_b)/R, \quad \eta = (r_a - r_b)/R,$$

As is well known, James calculated successfully the ground state energy of H_2^+ by using the function of the form of φ_g . Now we have three parameters, namely α , β and c . Since it is easily seen that 2α and 2β are just corresponding to ZR and $Z'R$ respectively, we assign the same values to them for the sake of simplicity, as shown in Table 4. c is determined by the usual Ritz method. The results of the calculation are shown in Table 6.

Table 6

R	$E_e(^3\Sigma_u^+)$	$E_e(^1\Sigma_u^+)$	A	$c(^3\Sigma_u^+)$	$c(^1\Sigma_u^+)$
1.0	-1.60656	-1.49251	0.11405	+0.1539409	+0.06550152
1.5	-1.46456	-1.27081	0.19375	+0.3508958	+0.09142185
2.0	-1.38686	-1.15330	0.23356	+0.6111767	+0.1396027

As for the $^3\Sigma_u^+$ state, the electronic energy values $E_e(^3\Sigma_u^+)$ in Table 6 are found to be almost identical with those of Table 5 (LCAO MO, $Z \neq Z'$), and the existence of the parameter c does not seem to play any significant role. On the other hand, definite improvements are found in $E_e(^1\Sigma_u^+)$ of Table 6 as compared with the corresponding values in Table 5. However, the fact that the values of c for $^1\Sigma_u^+$ are rather small seems to indicate that there would be some possibilities of further improvement by choosing the values of α and β more appropriately. Indeed, adopting a new set of these two parameters, $2\alpha=3$ and $2\beta=1$ at $R=2$, just corresponding to the last case of (a), we find that

$$E_e(^3\Sigma_u^+) = -1.34107, \quad c = +0.515597,$$

$$E_e(^1\Sigma_u^+) = -1.21097, \quad c = +0.278868.$$

Here is obtained a remarkable improvement for $E_e(^1\Sigma_u^+)$. Thus, the best combination of $E_e(^3\Sigma_u^+)$ and $E_e(^1\Sigma_u^+)$ at $R=2$, obtained by using the James-type molecular orbitals, is

$$\left. \begin{aligned} E_e(^3\Sigma_u^+) &= -1.38686, \quad (2\alpha=2.5, \quad 2\beta=1.5, \quad c=0.6111767), \\ E_e(^1\Sigma_u^+) &= -1.21097, \quad (2\alpha=3.0, \quad 2\beta=1.0, \quad c=0.2788684), \end{aligned} \right\} \quad (20)$$

and accordingly

$$A = 0.17589. \quad (R=2).$$

This is in tolerable agreement with $A \simeq 0.14$. In summarizing the results here obtained, we may say that not only the singlet-triplet separation but also the absolute energy value of the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states are estimated with rather good accuracy within the single configuration approximation, since the value of $E_e(^3\Sigma_u^+)$ in (20) is sufficiently close to the actual value, as already remarked. In this connection it is of interest to remind that we have already obtained rather good value of $E_e(^1\Sigma_u^+)$ at $R=2$, $E_e(^1\Sigma_u^+) = -1.20587$, by the one-center expansion method⁽¹⁾ in the single configuration approximation.

This value is definitely better than the best value -1.13555 of the LCAO MO approximation in (17) and that of the James-type approximation found in Table 6. We shall return to this point again in the last section of the present paper.

§ 3. He-He interaction energy

The calculation of the interaction energy between two normal helium atoms is one of the most fundamental problems in the quantum theory of molecular systems. If we try to tackle this problem by using the method of the molecular orbitals in the single configuration, it is natural to adopt one bonding orbital φ_g and one anti-bonding orbital φ_u and allot two electrons to each of these orbitals according to the Pauli principle. Explicitly, the wave function for the system consisting of two normal helium atoms separated by finite distance can be written

$$\Psi = (1/24)^{1/2} \sum_{\lambda} (-1)^{\lambda} P_{\lambda} [\varphi_g(1) \alpha(1) \varphi_g(2) \hat{\beta}(2) \varphi_u(3) \alpha(3) \varphi_u(4) \hat{\beta}(4)], \quad (21)$$

where P_{λ} is the operation permuting the electron coordinates, and α and $\hat{\beta}$ are the usual spin eigenfunctions. The functions, φ_g , φ_u , α and $\hat{\beta}$, are all supposed to be normalized to unity. We write the energy operator for the system as

$$H = \sum_{i=1}^4 H(i) + \sum_{i>j=1}^4 (1/r_{ij}) + (4/R) \quad (22)$$

where

$$H(i) = - (1/2) \Delta_i - (2/r_{ai}) - (2/r_{bi}). \quad (23)$$

Here $(4/R)$ is the Coulomb repulsive energy between two nuclei. Then the energy of the system is written out as

$$E = \int \Psi H \Psi d\tau = 2H_g + 2H_u + J_{gg} + J_{uu} + 4J_{gu} - 2K_{gu} + (4/R), \quad (24)$$

where the expressions of H_g , H_u , J_{gu} and K_{gu} are as given before in (9), (10), (11) and (12), respectively, and

$$J_{gg} = \iint \varphi_g(1) \varphi_g(1) (1/r_{12}) \varphi_g(2) \varphi_g(2) d\tau_1 d\tau_2, \quad (25)$$

$$J_{uu} = \iint \varphi_u(1) \varphi_u(1) (1/r_{12}) \varphi_u(2) \varphi_u(2) d\tau_1 d\tau_2. \quad (26)$$

Just as in the calculation on the hydrogen molecule in the preceding section, various approximations are obtained according to the ways of specifying the forms of φ_g and φ_u . Griffing and Wehner⁽¹⁰⁾ have made calculations corresponding to the cases (a-1) and (a-2). Murai⁽¹¹⁾ has performed a calculation on the present subject corresponding to the case (b) with considerable success. In the following we shall describe briefly two calculations carried out by the present author. The first one⁽¹²⁾ is the He-He version of the case (a-3) with $Z \neq Z'$ for the hydrogen molecule. In the second one⁽¹³⁾ we try to include the effect of polarization of the basic atomic orbitals by adding the $2p\sigma$

atomic orbital to the $1s\sigma$ atomic orbital. This idea is found in the earlier works of Dickinson¹⁴⁾ on H_2^+ and of Rosen¹⁵⁾ on H_2 . Griffing and Wehner¹⁰⁾ have also made use of this in order to calculate the van der Waals attraction energy between two normal helium atoms.

(I) LCAO MO approximation with $Z \neq Z'$

The molecular orbitals here used are the same as those in (a) of § 2 but it seems convenient to repeat them below:

$$\varphi_g = N_g(s_a + s_b) ; \sigma_g,$$

$$\varphi_u = N_u(s'_a - s'_b) ; \sigma_u,$$

$$s_a = (Z^3/\pi)^{1/2} \exp(-Zr_a), \quad s_b = (Z^3/\pi)^{1/2} \exp(-Zr_b),$$

$$s'_a = (Z'^3/\pi)^{1/2} \exp(-Z'r_a), \quad s'_b = (Z'^3/\pi)^{1/2} \exp(-Z'r_b).$$

The values of Z and Z' are determined largely through guess work similarly to that in (a-3) of the preceding section. Actual calculations were performed at three values of the internuclear distance R , 1.0, 1.5 and 2.0 au, and the results are summarized in Table 7, together with the values of Z and Z' adopted. $E(R)$ is the total energy of

Table 7

R	ZR	$Z'R$	$E(R)$	$V(R)$
1.0	2.25	1.25	-4.70584	0.98947 au (26.92 eV)
1.5	3.0	2.0	-5.32781	0.36750 au (10.0 eV)
2.0	3.5	3.0	-5.58131	0.11400 au (3.10 eV)

the He-He system and $V(R)$ is the repulsive potential energy defined by $E(R) - E(\infty)$. For convenience, we took $E(\infty) = -5.69531$ au in accordance with Griffing and Wehner¹⁰⁾ and Sakamoto and Ishiguro.¹⁶⁾ The result of the present calculation may be expressed conveniently in the following approximate formula:

$$V(R) = 8.58817 \exp(-2.16097R) \text{ au. } 1 \lesssim R \lesssim 2 \text{ (R in au).} \quad (27)$$

We have prepared Table 8 for the purpose of comparing the result of the present calculation with those of other calculations and the experimental data, where the figures listed in the column (4) are calculated from the above approximate formula (27). The column (3) indicates the result of Sakamoto and Ishiguro which is not significantly different from that of Griffing and Wehner under the restriction of $Z = Z'$, listed in the column (2). We see that the improvements achieved by dropping the severe restriction of equal effective charge $Z = Z'$ are rather remarkable in this case. Especially striking is the fact that the elaborated calculation of Rosen¹⁷⁾ yields very exaggerated values of the repulsive energy at small internuclear distance as shown in the column (1). Rosen started with two atomic orbitals of different effective charges but went forward by using the valence bond

method as contrasted with the molecular orbital method adopted here. If Rosen's calculation is numerically reliable, this situation seems to impose a serious question on the validity of the valence bond method for the present and other similar problems.

Table 8. He-He repulsive potential (in eV)

R (au)	(1)	(2)	(3)	(4)	(5)
0.8889	72.96	51.84	49.94	34.23	10.96
1.0	56.24	—	38.41	26.92	9.011
1.185	36.53	24.86	24.78	18.02	6.647
1.2	35.30	—	23.94	17.48	6.502
1.4	22.16	—	14.92	11.34	4.934
1.6	13.91	—	9.294	7.363	3.885
1.778	9.261	6.212	6.115	5.013	3.216
1.8	8.730	—	5.792	4.778	3.147
2.0	5.481	—	3.609	3.102	2.606

(1) Rosen¹⁷⁾(2) Griffing and Wehner¹⁰⁾(3) Sakamoto and Ishiguro¹⁶⁾ } (according to Table V of Sakamoto and Ishiguro)(5) Experimental result of
Amdur and Harkness¹⁸⁾ /

(4) Present calculation (I)

(II) Inclusion of polarization along the internuclear axis.

The primary purpose of the preceding calculation (I) was to diminish the large discrepancy between theory and experiment at small internuclear distance. This is the reason why we performed the calculation only over the range of $1 \lesssim R \lesssim 2$ au. However, the force range which is physically most important and of direct interest may probably be the van der Waals region and the neighboring inside. We shall report here an attempt of consistent quantum mechanical treatment of the interaction between two normal helium atoms from the repulsive region to the attractive van der Waals region. We use the following molecular orbitals:

$$\varphi_g = N_g [(s_a + s_b) + \lambda_g (p_a + p_b)]; \sigma_g, \quad (28)$$

$$\varphi_u = N_u [(s_a - s_b) + \lambda_u (p_a - p_b)]; \sigma_u, \quad (29)$$

where

$$\left. \begin{aligned} s_a &= (1s\sigma)_a = (Z^3/\pi)^{1/2} \exp(-Zr_a), \\ s_b &= (1s\sigma)_b = (Z^3/\pi)^{1/2} \exp(-Zr_b), \\ p_a &= (2p\sigma)_a = (Z^5/\pi)^{1/2} r_a \cos\theta_a \exp(-Zr_a), \\ p_b &= (2p\sigma)_b = (Z^5/\pi)^{1/2} r_b \cos\theta_b \exp(-Zr_b). \end{aligned} \right\} \quad (30)$$

λ_g and λ_u are the variable parameters and N_g and N_u are the normalization factors which depend on λ_g and λ_u respectively. To simplify the integrals, a fixed value of $Z=27/16$

was used commonly for $1s\sigma$ and $2p\sigma$ orbitals throughout the whole range of the internuclear separation. The above scheme of functions is essentially identical with that used by Griffing and Wehner¹⁰⁾ in their attempt to calculate the van der Waals attraction. The wave function of the system is given by (21) and the calculation goes just the same way as in (I). The dependence of $E(R)$ on λ_g and λ_u at each distance has been examined, as a rule, at intervals of 0.5 in significant figures. The results of the calculation are

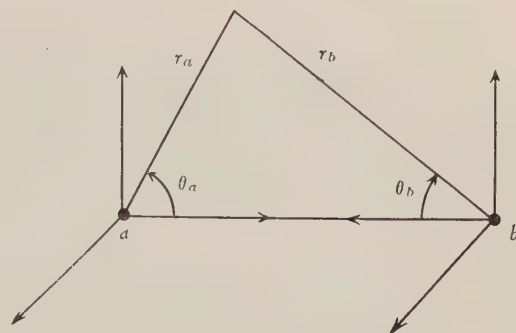


Fig. 1

summarized in Table 9. It is observed that λ_g is positive and λ_u is negative consistently for the whole range of the internuclear distance. This implies that the orbital φ_g has a tendency to concentrate in the inner region and the orbital φ_u wants to extend itself to

Table 9

R	Potential		λ_g	λ_u
(au)	(au)	(eV)		
1.185	0.79581	21.65	0.010	-0.225
1.778	0.20957	5.702	0.015	-0.085
2.370	0.053089	1.445	0.010	-0.040
2.963	0.012318	0.3352	0.010	-0.0245
3.556	0.002507	0.06821	0.0085	-0.0150
4.148	0.0004012	0.01092	0.0060	-0.0075
4.741	0.00003644	0.000992	0.0040	-0.0045
*5.877	-0.0000214	-0.0005823	0.0014	-0.0014

* The result of this last line is due to Griffing and Wehner.¹⁰⁾

the outer region. For four larger values of R in Table 9, 3.556, 4.148, 4.741 and 5.877, the well-known Slater-Kirkwood potential formula gives 2.314×10^{-3} au, 4.222×10^{-4} au, 3.466×10^{-5} au and -2.696×10^{-5} au, respectively, as the potential energy values. On the other hand, the repulsive energies of 21.65 eV at $R=1.185$ au and 5.702 eV at $R=1.778$ au are favorably compared with the corresponding values of Griffing and Wehner ($\lambda_g=\lambda_u=0$), 24.86 eV and 6.212 eV respectively, where they failed to improve the values by varying the effective charge parameter Z . It is instructive to note that the same kind of deformations of the molecular orbitals in the single configuration approximation can cover rather effectively the whole range of interaction between two normal helium atoms, from the repulsive region to the van der Waals region, with tolerable accuracy.

§ 4. Ethylene molecule

The ASMO LCAO method in its usual form utterly fails to give properly the value of the singlet-triplet separation of the excited B_{1u} states of the ethylene molecule. On the other hand, in treating theoretically this molecule by the method of atoms in molecules, Moffitt⁽¹⁹⁾ succeeded to obtain remarkably good agreement between theory and experiment. This success seems to be one of the cornerstones of his method and his philosophy.

We shall treat the ethylene molecule in its stable form only, that is to say, assuming it to be planar. In the π -electron approximation our subject is essentially a two-electron problem. If we prepare one bonding molecular orbital ϕ and one anti-bonding molecular orbital ϕ^* for the two electrons, the wave function of the three lower states are given as follows in the single configuration approximation :

$$\Psi_N(^1A_g) = \phi(1)\phi(2), \quad (31)$$

$$\Psi_T(^3B_{1u}) = (1/\sqrt{2})[\phi(1)\phi^*(2) - \phi^*(1)\phi(2)], \quad (32)$$

$$\Psi_V(^1B_{1u}) = (1/\sqrt{2})[\phi(1)\phi^*(2) + \phi^*(1)\phi(2)], \quad (33)$$

where ϕ and ϕ^* are assumed to be normalized to unity. The explicit forms of ϕ and ϕ^* in the conventional LCAO MO approximation are

$$\phi = N[(2p\pi)_a + (2p\pi)_b], \quad \phi^* = N^*[(2p\pi)_a - (2p\pi)_b], \quad (34)$$

where $(2p\pi)_a$ and $(2p\pi)_b$ are $2p\pi$ atomic orbitals at the carbon nuclei a and b , respectively. The atomic orbitals contain the effective charge parameter, say Z . Usually the value of Z is fixed *ab initio* and the same value is used commonly for Ψ_N , Ψ_T , and Ψ_V . Roughly speaking, this stage of approximation corresponds to the case (a-1) of § 2. Moser⁽²⁰⁾ and others carried out the calculations in this approximation. An interesting calculation corresponding to the case (a-2) of § 2 has been performed by Murai.¹¹ The results of these calculations are found in Table 11 and we see the results are not encouraging, especially revealing the notorious defect of exaggerating grossly the singlet-triplet separation of the B_{1u} states. It is highly desirable to perform the calculation which corresponds to the case (a-3) ($Z \neq Z'$) of § 2 by using the orbitals;

$$\phi = N[(2p\pi)_a + (2p\pi)_b], \quad \phi^* = N^*[(2p\pi)_{a'} - (2p\pi)_{b'}], \quad (35)$$

where primes in ϕ^* indicate that we use different effective charges for ϕ and ϕ^* . However, if we try to make such a calculation non-empirically, we have to devote a large amount of labor to the numerical evaluation of various molecular integrals. The same is true if we want to make a calculation similar to the case (b) of § 2 on the ethylene molecule. Let us remind, however, that the one-center expansion method has been applied to the $^1\Sigma_u^+$ state of H_2 even more successfully than the LCAO MO method with $Z \neq Z'$, as remarked in the last paragraph of § 2. Then it is natural to try to apply the one-center method to the ethylene molecule as a substitute for more orthodox calculations to be performed in the future.

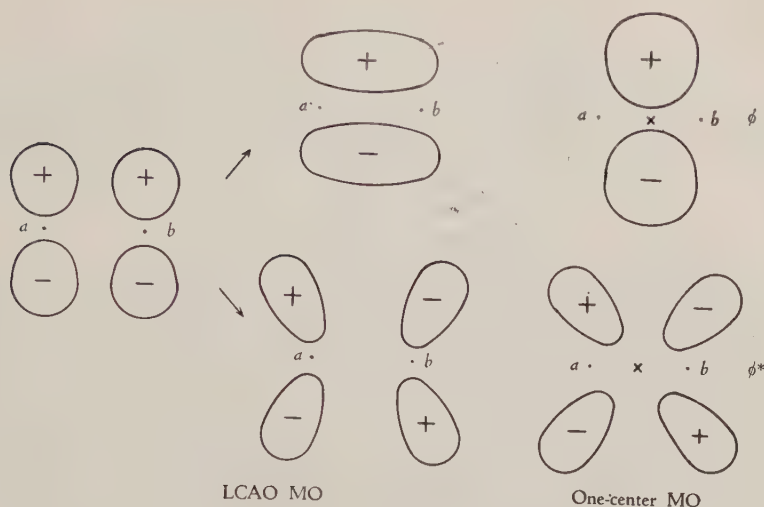


Fig. 2

The simplest choice of the one-center molecular orbitals for the present problem would be to take

$$\phi = (2p\pi) = R_p(r) S_{11}(\theta, \varphi), \rightarrow p \quad (36)$$

$$R_p(r) = N(2, \zeta) r \exp(-\zeta r),$$

$$S_{11}(\theta, \varphi) = (1/2)^{1/2} [Y_{1,-1}(\theta, \varphi) + (-1) Y_{1,+1}(\theta, \varphi)],$$

$$Y_{1,\pm 1}(\theta, \varphi) = \mp (3/8\pi)^{1/2} \sin \theta \exp(\pm i\varphi),$$

$$\phi^* = (3d\pi) = R_d(r) S_{21}(\theta, \varphi), \rightarrow d \quad (37)$$

$$R_d(r) = N(3, \delta) r^2 \exp(-\delta r),$$

$$S_{21}(\theta, \varphi) = (1/2)^{1/2} [Y_{2,-1}(\theta, \varphi) + (-1) Y_{2,+1}(\theta, \varphi)],$$

$$Y_{2,\pm 1}(\theta, \varphi) = \mp (15/8\pi)^{1/2} \sin \theta \cos \theta \exp(\pm i\varphi).$$

Here the reference center of the electron coordinates is located at the middle point between two carbon nuclei. (See Fig. 2) ζ and δ are the variable exponent parameters and $N(2, \zeta)$ and $N(3, \delta)$ are the normalization factors for the respective radial functions. By using simplified notations, p and d , indicated above, the wave functions of the three states in question can be written

$$\Psi_N(^1A_g) = p(1)p(2), \quad (38)$$

$$\Psi_T(^3B_{1u}) = (1/\sqrt{2}) [p(1)d(2) - d(1)p(2)], \quad (39)$$

$$\Psi_V(^1B_{1u}) = (1/\sqrt{2}) [p(1)d(2) + d(1)p(2)]. \quad (40)$$

The Hamiltonian for the system may be written

$$H = T(1) + T(2) + H_0(1) + H_0(2) + (1/r_{12}) \quad (41)$$

where $T(\nu)$ is the kinetic energy of electron ν , $H_0(\nu)$ is the mutual potential energy of electron ν and the single-bonded H_2C-CH_2 framework, and $1/r_{12}$ is the repulsive potential between electron 1 and 2 (in the atomic units). Various expressions have been used for $H_0(\nu)$ and we shall adopt tentatively the simplest of them after Labhart, namely,

$$H_0(\nu) = -Z(1/r_{a\nu} + 1/r_{b\nu}), \quad (42)$$

where $r_{a\nu}$ and $r_{b\nu}$ are the distances of electron ν from the carbon nuclei a and b , respectively. As for the values of the parameter Z , Labhart assumed two values, 3.25 and 2.04. Correspondingly we adopt here two values of Z , 3 and 2, and see what happens in the relative positions of the three energy levels in question.

In the present one-center method the molecular orbitals, ϕ and ϕ^* , are both centered on the middle point between two carbon nuclei and consequently the calculation offers no troubles. For the sake of convenience, the carbon-carbon distance is assumed to be 2.5 au ($\simeq 1.323 \text{ \AA}$). The parameters, ζ and δ , are determined in the following way. First we consider the case where one electron occupies the orbital $\phi = (2p\pi)$ and ζ is chosen so that the energy of the system, $(2p\pi | T + H | 2p\pi)$, is minimized. Actual minimization process was performed only at intervals of 0.1 and the results are

$$(Z=2) \quad \zeta = 1.1 \quad \text{and} \quad (Z=3) \quad \zeta = 1.4.$$

These values are used for the p orbital in $\mathcal{U}_T(^3B_{1u})$ and $\mathcal{U}_T(^1B_{1u})$. Next, as for $\mathcal{U}_N(^1A_g) = p(1)p(2)$, we calculate the energy of this two-electron system and the values of ζ are determined to be

$$(Z=2) \quad \zeta = 1.0 \quad \text{and} \quad (Z=3) \quad \zeta = 1.3.$$

Corresponding values of the energy $E_N(^1A_g)$ are

$$(Z=2) \quad E_N(^1A_g) = -2.00878 \text{ au} \quad \text{and} \quad (Z=3) \quad E_N(^1A_g) = -3.89346 \text{ au}.$$

Finally we calculate $E_T(^3B_{1u})$ and $E_T(^1B_{1u})$ by varying the parameter of the $3d\pi$ orbital and the results are shown in Table 10.

Table 10

Z	ζ	δ	$E_T(^3B_{1u})$	$E_T(^1B_{1u})$
2	1.1	0.9	-1.75293	-1.68484
		1.0	-1.79119	-1.70796
		1.1	-1.79943	-1.70220
		1.2	-1.79197	-1.68233
3	1.4	1.3	-3.59534	-3.48544
		1.4	-3.62030	-3.49655
		1.5	-3.62871	-3.49237
		1.6	-3.61994	-3.47240

We pick up the best combinations of $E_T(^3B_{1u})$ and $E_V(^1B_{1u})$ from Table 10 as follows;

$$\begin{aligned} (Z=2) \quad & \begin{cases} E_T = -1.79943 \text{ au} & (\zeta=1.1, \delta=1.1), \\ E_V = -1.70796 \text{ au} & (\zeta=1.1, \delta=1.0), \end{cases} \\ (Z=3) \quad & \begin{cases} E_T = -3.62871 \text{ au} & (\zeta=1.4, \delta=1.5), \\ E_V = -3.49655 \text{ au} & (\zeta=1.4, \delta=1.4). \end{cases} \end{aligned}$$

Then we can now calculate the relative positions of the three energy levels of the system, $^1B_{1u}$, $^3B_{1u}$ and ^1A_g , referring to the value of $E_N(^1A_g)$ given before. The results are shown in Table 11, together with those of various other calculations and observed data. As is seen from Table 10 and 11, in spite of the drastic changes in absolute values of energy between the cases of $Z=2$ and $Z=3$, the relative position of the energy levels suffers comparatively small changes. The situation does not alter if we put a certain amount of negative charge on the middle point between two carbon nuclei. This modification seems to be of some use for obtaining reasonable value for the ionization energy of the molecule but too much elaboration on this point does not seem to be worthy. After all, if our simplified assumption (42) for $H_0(\nu)$ is acceptable, at least provisionally, the results exhibited in Table 11 may be found rather interesting. The result of the present simple calculation seems to indicate good possibility of the successful orbital approach to the present subject, in spite of recent critiques of Moffitt and others.

Table 11. Electronic states of ethylene* (in eV)

State	ASMO ^a	Murai ^b	Ohno-Itoh ^c	Moffitt ^d	Obs. ^a	This paper	
						$Z=2$	$Z=3$
$V(^1B_{1u})$	11.4	11.2	7.7	7.3	7.6	8.2	10.8
$T(^3B_{1u})$	2.8	4.6	5.4	5.5	6.4	5.7	7.2
$N(^1A_g)$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$V-T$	8.6	6.6	2.3	1.8	1.2	2.5	3.6

^a See reference 20.

^b See reference 21.

^c K. Ohno and T. Itoh, J. Chem. Phys. 23 (1955), 1468.

^d See reference 19.

* The internuclear distance of 1.353 Å is used in *a*, *b*, *c* and *d*, while in the present calculation the value of 1.323 Å is adopted.

§ 5. Discussions

(a)

It has been stated in (a-3) of § 2 that the leading motif of the present work is to give the freedoms of separate deformations to the bonding and anti-bonding molecular orbitals. The importance of such a procedure was first noted for the hydrogen molecular ion by Coulson²³⁾ in 1937. Roughly speaking, the bonding orbital tends to contract

inwardly and, on the contrary, the anti-bonding orbital wants to extend itself outwardly, these tendencies being understood most easily from the united-atom point of view.

In the present calculations we have used several kinds of device to give such freedoms to the molecular orbitals. The first of them is to assign distinct effective charges to the bonding and anti-bonding orbitals in the LCAO MO method. This device is quite successful in the calculation of the repulsive potential between two normal helium atoms, as described in (I) of § 3, and gives satisfactory result concerning the $^3\Sigma_u^-$ state of the hydrogen molecule, as reported in (a-3) of § 2. It fails, however, to estimate properly the energy of the $^1\Sigma_u^+$ state, giving too large value for the singlet-triplet separation of the Σ_u^+ states. Fortunately we have succeeded to overcome this difficulty by employing another kind of molecular orbital called James-type tentatively in (b) of § 2. Let us repeat the expressions here, for the sake of convenience :

$$\varphi_g \sim (1 + c\gamma^2) \exp(-\alpha\hat{r}), \quad \varphi_u \sim \gamma \exp(-\beta\hat{r}),$$

$$\hat{r} = (r_a + r_b)/R, \quad \gamma = (r_a - r_b)/R. \quad (43)$$

Now let us examine the bearing of the parameters α , β and c a little more closely than in § 2. In Table 6 we notice that the values of c are remarkably different for $^3\Sigma_u^-$ and $^1\Sigma_u^+$. At $R=2$, for example, $c=0.6111767$ for $^3\Sigma_u^-$ and $c=0.1396027$ for $^1\Sigma_u^+$ in the case of $(2\alpha=2.5, 2\beta=1.5)$. What is meant by this large difference?

To answer this question, let us digress briefly to recall that it is usually told in such a way that in the single configuration approximation of the ASMO method the wave function which consists essentially of the products of one-electron orbitals gives the correlation between electrons with parallel

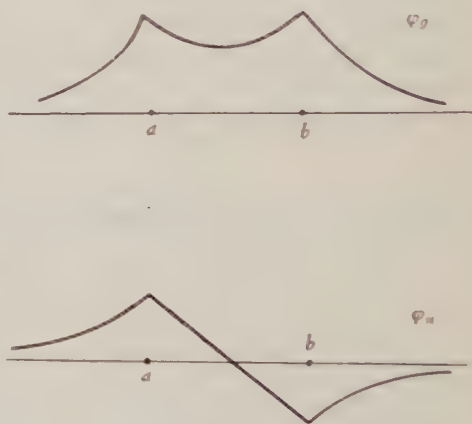


Fig. 3

spins because of the antisymmetry requirement but cannot include properly the correlation effect between electrons with opposite spins. Probably this is the reason why we can be successful for the $^3\Sigma_u^+$ state but not for the $^1\Sigma_u^+$ state of the hydrogen molecule in the LCAO MO method with two parameters of Z and Z' . Overlapping of the two electron orbitals would be too large for the $^1\Sigma_u^+$ state with two electrons of opposite spins, while it is moderated appropriately by the antisymmetry of the wave function for the $^3\Sigma_u^-$ state. We shall now return to our James-type orbitals. The parameters α and β correspond to Z and Z' of the LCAO MO approximation but here we have an additional parameter c , by which we can adjust further the degree of spatial overlapping between the two electron orbitals. As is seen from the expression of φ_u in (43), small c means that the electron distribution tends to accumulate in the space between the two nuclei and, on the contrary, large value of c implies that the electron concentrates at the positions

of the nuclei. For the ${}^1\Sigma_u^+$ state we have small value of c in order to reduce the error due to the interaction between electrons with opposite spins. For the ${}^3\Sigma_u^+$ state, however, the wave function $\varphi_g(r_1)\varphi_u(r_2) - \varphi_u(r_1)\varphi_g(r_2)$ vanishes automatically when $r_1=r_2$ and then we are able to increase the value of c , letting the electron feel the nuclear attraction more effectively without worrying too much about the electron-electron correlation. (Actually, the value of c is determined by the Ritz method.) As is noted in (b) of § 2, however, $c=0.1396027$ for ${}^1\Sigma_u^+$ in the case of ($2\alpha=2.5$, $2\beta=1.5$, $R=2$) seems to be too small, probably reflecting the fact that the choice of α and β is not proper and the parameter c is forced to be too small to separate φ_g and φ_u spatially, in order to compensate the loss due to the wrong choice of α and β . Indeed, if we contract φ_g a little more by taking $2\alpha=3$ and extend φ_u by taking $2\beta=1$, instead of $2\alpha=2.5$ and $2\beta=1.5$, we obtain the improved value of $E_e({}^1\Sigma_u^+) = -1.21097$ au with $c=0.2788684$ at $R=2$, this value being considerably larger than the former value of 0.1396027.

We may say that the deformation afforded by the parameters (Z , Z') or (α , β) is essentially of one-electronic in nature. The well-known result on the one-electron system of H_2^+ supports this point of view. The demand for the flexibility owing to the parameter c may be called as partly one-electronic and partly two-electronic in view of the above considerations. Anyhow, it seems to be reasonable to regard these deformations as of *inter-atomic* nature rather than of *intra-atomic* nature, according to the terminology of Moffitt.

(b)

Making an analysis of certain observed and calculated features of the oxygen molecule, Moffitt⁽²⁴⁾ concluded that it is mainly in its inability correctly describing the term values of atomic (stationary and valence) states that the ASMO method breaks down. As a result of this analysis, a different method, the method of atoms in molecules, was put forward by Moffitt.⁽²⁵⁾ The basis of this new method is to separate the problems of atomic from those of molecular structure. Moffitt's argument is ingenious and quite successful in some cases but it seems to be neither definitive nor unambiguous. He starts with the analysis of the asymptotic behavior of the wave function of molecular system in the limit of infinite separation. In view of the results of the present paper, however, it is clear that we are not always justified in drawing definite criteria for "molecular" orbitals from such a procedure. For example, the wave functions of the lowest ${}^3\Sigma_u^+$ and ${}^1\Sigma_u^+$ state of H_2 consisting of the James-type orbitals are rather good at the internuclear separation of actual molecular configuration but they are bound to behave very incorrectly at the infinite separation, as is readily seen in (43). More simple and impressive examples are found in the successful applications of the one-center expansion method to molecular systems. Recently the present author⁽²⁶⁾ calculated the repulsive potential between two normal helium atoms at small distance by the united-atom approximation. The molecular orbitals used are

$$\varphi_g = (1s\sigma) = N(1, \zeta) \exp(-\zeta r) Y_{00},$$

$$\varphi_u = (2p\sigma) = N(2, \eta) r \exp(-\eta r) Y_{10}.$$

The origin of electron coordinates is located at the middle point between two nuclei as pictured in Fig. 4. Even at the distance of $R=1.0$ au these seemingly very crude molecular orbitals work definitely better than the elaborate valence bond wave function of Rosen.¹⁷⁾ It is to be noted that Rosen's wave function is

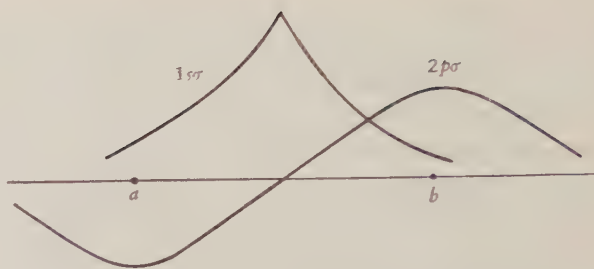


Fig. 4

excellent at infinite separation, while the united-atom wave function breaks down completely there. In addition, even at small separation one-center wave function describes only very crudely the electrons in the "atomic" region around nuclei as is seen from Fig. 4, while Rosen's function is accurate in the "atomic" region. The unexpected success of the one-center molecular orbitals strongly suggests that in calculating the repulsive energy between two helium atoms at small distance the deformations of the molecular orbitals over the whole molecular dimension are essentially important. Matters are quite similar for the treatment⁽¹⁾ of the lower excited states of the hydrogen molecule by the one-center expansion method. For the $^1\Sigma_u$ state at $R=2$ we have used the wave function,

$$\Psi(^1\Sigma_u^+) = (1/\sqrt{2})[\varphi_g(1)\varphi_u(2) + \varphi_u(1)\varphi_g(2)],$$

where

$$\varphi_g = 0.6614319[(1s\sigma; 1) + 0.51260(4s\sigma; 3) + 0.2707095(4d\sigma; 3)],$$

$$(ns\sigma; \zeta) = N(n, \zeta) r^{n-1} \exp(-\zeta r) Y_{00},$$

$$(nd\sigma; \zeta) = N(n, \zeta) r^{n-1} \exp(-\zeta r) Y_{20},$$

$$N(n, \zeta) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2},$$

$$\varphi_u = (2p\sigma; \eta) = N(2, \eta) r \exp(-\eta r) Y_{10}.$$

Again, the center of the electron coordinates is located at the middle point between two nuclei. This function yields the value of $E(^1\Sigma_u^-) = -1.205872$ ($\eta=0.5$) as the electronic energy of the $^1\Sigma_u$ state at $R=2$, as remarked in the last part of (b) of § 2. This result is favorably compared with the results of the LCAO MO approximation, for example, -1.08121 in Table 3 ($Z=Z'=1$) and -1.11140 in Table 5 ($Z \neq Z'$). Thus we have been able to obtain rather good energy value of the $^1\Sigma_u$ state by the one-center expansion method, in spite of the apparent crudeness of the wave function not only in the large internuclear separation but also in the vicinity of nuclei at small distance. The reason for this success is essentially the same as in the calculation based upon the James-type molecular orbitals: if we give appropriate flexibilities to molecular orbitals and utilize the whole space around the molecular system to reduce the error due to the electron correlation, we can obtain rather good results even within the single configuration approximation. Similar situation may naturally be expected in the case of the $^3B_{1u}$ and

$^1B_{1u}$ states of the ethylene molecule. A preliminary calculation reported in § 3 seems to confirm this expectation. The same would be expected also for the $^3\Sigma_u^+$ and $^3\Sigma_u^-$ states of the oxygen molecule.

(c)

The failure of the conventional ASMO LCAO approximation does not necessarily mean the break-down of the useful concept of "molecular orbital" itself. The principal aim of the present paper is to testify this by presenting several examples.

Needless to say, it is absurd to stick to the orbital approach and remain within the single configuration approximation spending too much labor, if we are supplied with new efficient and reliable calculation schemes by giving up the simple orbital description. The merit of the various semi-empirical methods, such as of Moffitt and of Pariser and Parr,²⁶⁾ is that they enable us to treat efficiently rather complicated problems with reasonable labor. Also in regard to the so-called non-empirical method, if we can improve the result of the first approximation sufficiently by including only a few configuration interactions, it is meaningless to try to stay within the single configuration approximation by elaborating the forms of orbitals.

In this connection, however, it is to be noted that the new method of Moffitt or something like that is very useful in some cases but, after all, never constitutes a rigorous theory by which we are guaranteed to reach the final truth from the theoretical side. On the other hand, nothing prevents us, at least in principle, to reach the final goal by using the conventional ASMO method with configuration interactions. But, actually, here arises the serious difficulty of poor convergency in the procedure of configuration superposition. A typical and very instructive example for this is found in the work of Taylor and Parr²⁷⁾ on the ground state energy of the helium atom. We learn from their results that it is very difficult to compensate the error due to the wrong choice of the starting single configuration by the procedure of configuration superposition. We see that if we start from the single configuration $(1s)^2$ ($E = -2.8477$ au), we reach $E = -2.8719$ au at best by superposing four configurations, $(1s)^2$, $(2p)^2$, $(3d)^2$ and $(4f)^2$, while single open shell configuration $(1s1s')$ yields $E = -2.8757$ au and with four configurations, $(1s1s')$, $(2p)^2$, $(3d)^2$ and $(4f)^2$, we can reach an excellent value of $E = -2.8974$ au, experimental value being $E = -2.9035$ au. Murai²⁸⁾ has noticed that matters would be quite similar also for molecular calculations. If it is the case, effort to look for the good wave function in the single configuration, such as described in the present paper, will become necessary for future calculations aiming at rapid convergency and high accuracy.

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On the Representations of Field Quantities

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In this paper we study what kind of mathematical framework is adequate to the future quantum theory of fields, which is physically correct and mathematically rigorous. From the physical point of view, we assume that the field quantities form a $*$ -algebra and that the states are linear functionals on it. Field quantities must have many physical properties, and so the $*$ -algebra must have corresponding properties, which we shall describe in a mathematically precise manner. From these properties we show that this $*$ -algebra can be represented by an operator algebra in a separable Hilbert space, and that states are closely related to vectors of this space.

§ 1. Introduction

In quantum mechanics it is assumed that the set of all state vectors of any physical system forms a separable Hilbert space, and that any physical quantity can be represented by an operator in this space. In order to study quantum mechanics with mathematical rigour, these are the most essential assumptions, on which quantum mechanics is systematized to be a complete physical theory. In general, the above assumptions are accepted also in the quantum theory of fields, yet it is open to question whether they are quite adequate or not. For example, if any interaction of two fields causes creation and annihilation of particles, the Hilbert space cannot be separable because the system has an infinite number of degrees of freedom¹⁾. Further, though field operators $\phi(x)$, etc., play very essential roles in the usual field theory, the mathematical contents and roles of these operators are not yet clarified, and they are customarily considered to be merely symbolic [2], p. 13]. Some authors assert, therefore, that the above assumptions are not adequate and that this is the reason why attempts to build a rigorous mathematical basis for the quantum theory of fields within the framework of a Hilbert space always end in unsatisfactory results¹⁾. This assertion may be correct to a certain extent, but even if it is the case, the problem, what kind of mathematical framework is adequate, has hardly been studied yet. To solve this problem is the main purpose of this paper.

Though the *renormalization* procedure is still mathematically incomprehensible, the usual quantum theory of fields has succeeded in some respects by means of this procedure. Therefore we may say that, in future, we shall be able to build a satisfactory quantum theory of fields which is physically correct and mathematically rigorous, and that quantum mechanics and the usual quantum theory of fields show some signs of correctness which will survive in the expected future theory. Now we must study what parts of the usual

quantum theory of fields will remain valid in the future theory. For this purpose, we put a set of assumptions each of which seems to us to be very natural from the physical point of view, especially from the standpoint of the usual quantum theory of fields, and we study to what conclusions these assumptions lead. We treat fundamental but rather formal problems in this paper, and characteristic problems of the *field theory*, which will be connected with the divergence difficulties, will be treated in the next paper.

In quantum mechanics we may consider two representations, the Schrödinger and the Heisenberg representations, but they are mathematically equivalent and are transformed into each other by some unitary transformations. We do not know, however, to what extent holds the correspondence between quantum mechanics and the quantum theory of fields, and so it is necessary to decide in which representation we must start our considerations. This problem will be equivalent to the following: which are more essential, physical quantities or states? In quantum mechanics it seems to us that state vectors are more essential than physical quantities, but, in the usual quantum theory of fields, especially in view of the method of calculations of this theory, we may say that physical quantities play more essential roles than states. In fact, the kernel of the method of second quantization which connects the two theories, is to regard state vectors in quantum mechanics as operators in the quantum theory of fields. Thus, we may say that in quantum mechanics states play an essential role, while in the quantum theory of fields physical quantities are more essential. Therefore, we believe that in the quantum theory of fields physical quantities and algebraic operations for these quantities are most essential and that they will remain valid in the future theory. But, as we have stated in the beginning of this section, it will be inadequate to accept field operators themselves as physical quantities and, at the same time, to accept usual algebraic operations for them. We can, however, construct an operator ϕ_i from field operators $\phi(x)$, as follows: Let $\gamma(x)$ be any appropriate function and put $\phi_i = \int \phi(x) \gamma(x) dx$, then this ϕ_i can be considered as something like an average of $\phi(x)$ and we can treat it more consistently than $\phi(x)$ [2], p. 15]. In this paper, therefore, we treat only these consistent operators and we call them *field quantities* in contrast to field operators $\phi(x)$, etc.

To accept the usual algebraic operations for field quantities will be equivalent to assume that the set of field quantities forms a $\ast$ -algebra $\mathfrak{A}$. In any state, we shall be able to measure any field quantity and to get a definite mean value, namely an expectation value, and hence we assume that a state is a *linear functional* on the set of field quantities. Thus the objects of our study are the $\ast$ -algebra and linear functionals on it. From physical requirements field quantities must have many properties, which we shall describe in a precise way in terms of the mathematical conditions to be satisfied by the $\ast$ -algebra $\mathfrak{A}$. Of course, we cannot say that the correspondence of the physical properties

¹ In quantum mechanics physical quantities are often assumed to be self-adjoint, and then the product of any two physical quantities is not necessarily admitted, but, in quantum theory of fields, operators which are not self-adjoint play an essential role (creation and annihilation operators, etc.). We do not, therefore, assume in this paper that all field quantities are self-adjoint, and so we can assume consistently that the product of any two is admissible.

of field quantities to the mathematical forms of assumptions is determined uniquely. But we believe that these assumptions are very suitable for the corresponding physical requirements. Furthermore, it will be almost inevitable from the standpoint of present-day physics to put these assumptions or mathematically equivalent ones, and if we do not put these assumptions, we shall be in a very difficult situation (not only mathematically but physically). On these assumptions we shall show that $\mathfrak{A}$ can be represented by an operator algebra in a separable Hilbert space, and that, on a set of commutative self-adjoint quantities, any state can be represented by a vector of the Hilbert space.

From the standpoint of mathematics, the main problem in this paper is that of representations of $*$ -algebras. There are many studies concerning representations of the Banach algebras and their relations to quantum mechanics³⁾, but the fundamental notion in these theories, namely that of a *norm*, seems to us to be physically unacceptable. Indeed, in quantum mechanics and in quantum theory of fields, many unbounded operators play a most important role. To the author's opinion, the most fundamental property of field quantities is shown in the fact that we can give an expectation value to any quantity in any state, and so we use this property exclusively. In this respect, we may say that we use *semi-norms* instead of *norms* in the Banach algebra.

§ 2. Field quantities and states

Let $\mathfrak{A}$ be the set of field quantities of a given physical system, and $a, b, \dots$ be its elements. Let $\mathfrak{K}$ and $\mathfrak{R}$ be the complex and real number fields respectively. As stated in § 1, we assume that the usual algebraic operations for field quantities are adoptable in our case. Namely, we assume that, if $\alpha \in \mathfrak{K}$ and $a, b \in \mathfrak{A}$, there are defined $a+b$, ab and αa in $\mathfrak{A}$, and $\mathfrak{A}$ is an algebra over $\mathfrak{K}$ [4], p. 11]. In quantum mechanics there is an identity operator I in a Hilbert space, and if we want to regard any *c-number* α as a physical quantity, we must replace it with an operator αI . Therefore we assume that there is a unit element e in $\mathfrak{A}$. In the usual theory every field quantity has an adjoint, and this fact has a very essential meaning. For example an adjoint of a creation operator is an annihilation operator. Thus we assume the existence of an adjoint a^* of every element a in $\mathfrak{A}$ [4], p. 499]. Summing up these assumptions we put

Assumption 1. $\mathfrak{A}$ is a $*$ -algebra over $\mathfrak{K}$ with a unit element e .

Here a $*$ -algebra is an algebra in which every element a has an adjoint a^* subject to the conditions:

- (i) $(a^*)^* = a$,
- (ii) $(a+b)^* = a^* + b^*$,
- (iii) $(ab)^* = b^* a^*$,
- (iv) $(\alpha a)^* = \bar{\alpha} a^*$ ($\alpha \in \mathfrak{K}$ and $\bar{\alpha}$ is the conjugate complex number to α).

An element $a \in \mathfrak{A}$ is said *self-adjoint* if $a = a^*$, and it is clear that the set $\mathfrak{A}_{sa}$ of all self-adjoint elements of $\mathfrak{A}$ is a vector space over $\mathfrak{R}$, and that every element $a \in \mathfrak{A}$ is uniquely expressed as the sum $a = a_1 + ia_2$, where both a_1 and a_2 are self-adjoint.

Let $f, g, \dots$ be *states* of the physical system under consideration, and $\mathfrak{S}_0$ be the set

of these states. We assume that measuring any field quantity $a \in \mathfrak{A}_\alpha$ in any state $f \in \mathfrak{Z}$, we can get a definite mean value called *expectation value*, and can denote it by $f(a)$. Further, we assume that

$$f(\alpha a + \beta b) = \alpha f(a) + \beta f(b), \quad \alpha, \beta \in \mathbb{R},$$

namely the state f defines a linear functional on $\mathfrak{A}_{\text{sa}}$, and that if we know the value $f(a)$ for all $a \in \mathfrak{A}_{\text{sa}}$, the state f is completely defined. So we put

Assumption 2. Any state f is a linear functional on $\mathfrak{A}_{\text{sa}}$ and satisfies the following conditions :

- (i) $f(e) = 1$,
- (ii) $f(a^2) \geq 0$ for all $a \in \mathfrak{A}_{\text{sa}}$,
- (iii) if $a \approx 0$, there is a state f in which $f(a) \approx 0$.

As $a = (1/2)(e + a) - (1/2)(e - a)$, it is clear that $f(a)$ is real for all $a \in \mathfrak{A}_{\text{sa}}$. The condition (i) assures the normalization of states, and the condition (ii) may be interpreted as follows: if $a \in \mathfrak{A}_{\text{sa}}$, a^2 is non-negative in a sense [see § 3]. From the condition (iii), we find that when $a \approx b$, there is a state f in which $f(a) \approx f(b)$, and therefore we can distinguish any field quantity from another by their expectation values in some appropriate state.

For any linear functional on $\mathfrak{A}_{\text{sa}}$ we can show

Lemma 2.1. If $f \approx 0$ is a linear functional on $\mathfrak{A}_{\text{sa}}$ and $f(a^2) \geq 0$ for all $a \in \mathfrak{A}_{\text{sa}}$, then $f(e) \approx 0$.

Proof. As $f \approx 0$, there is an element $a \in \mathfrak{A}_{\text{sa}}$ for which $f(a) \approx 0$. Let $f(e) = 0$, then we have for any $\alpha \in \mathbb{R}$

$$0 \leq f[(\alpha e - a)^2] = f(\alpha^2 e - 2\alpha a + a^2) = f(a^2) - 2\alpha f(a),$$

from which follows $f(a) = 0$, and we have a contradiction.

Q.E.D.

Putting $(f + g)(a) = f(a) + g(a)$ and $(\alpha f)(a) = \alpha f(a)$ for any $f, g \in \mathfrak{Z}$, and $\alpha \in \mathbb{R}$, we can construct a real linear space

$$\mathfrak{F}_r = \{f; f = \sum_{i=1}^n \alpha_i f_i\}.$$

Let $f \in \mathfrak{F}_r$ and $f(a^2) \geq 0$ for all $a \in \mathfrak{A}_{\text{sa}}$, then $f(e) \approx 0$ by Lemma 2.1, and putting $f' = (1/f(e))f$, we can define a linear functional $f' \in \mathfrak{F}$ which satisfies the conditions (i) and (ii) in Assumption 2. Let $\mathfrak{Z}$ be the set of all these linear functionals. It is clear that $\mathfrak{Z}_0 \subset \mathfrak{Z}$, and we call every element $f \in \mathfrak{Z}$ also a state. In quantum mechanics, we can define that, for any vector ζ^h , $f(a) = (\zeta^h, a \zeta^h)$ (ζ^h, ζ^h) is a state in our sense. Let the set of these states be $\mathfrak{Z}_0$. Then constructing $\mathfrak{Z}$ by the above method, we can easily show that $\mathfrak{Z}_0 \approx \mathfrak{Z}$ in general. By using $\mathfrak{Z}$ or $\mathfrak{Z}_0$, there will be no serious differences, and so we use $\mathfrak{Z}$ instead of $\mathfrak{Z}_0$ only for brevity's sake.

Since every $a \in \mathfrak{A}$ is expressed as the sum $a = a_1 + ia_2$, $a_1, a_2 \in \mathfrak{A}_{\text{sa}}$, we can extend any $f \in \mathfrak{F}_r$ on $\mathfrak{A}_{\text{sa}}$ to a linear functional on $\mathfrak{A}$ by the equation $f(a) = f(a_1) + if(a_2)$. Let $\mathfrak{F}$ be a complex linear space which is generated by these linear functionals on $\mathfrak{A}$. If we identify $f \in \mathfrak{F}_r$ with the corresponding $f \in \mathfrak{F}$, it is clear that $\mathfrak{F}_r \subset \mathfrak{F}$.

We shall now proceed to the duality of $\mathfrak{A}$ and $\mathfrak{F}$. Let A and B be two linear space over a number field K . We say that A and B are dual to each other, if there is a bilinear mapping $(a, b) \rightarrow T(a, b) \in K$, $a \in A$, $b \in B$, which satisfies the following conditions:

- (i) for any $a \neq 0$ in A , there is an element b in B , for which $T(a, b) \neq 0$,
- (ii) for any $b \neq 0$ in B , there is an element a in A , for which $T(a, b) \neq 0$ [5], Chap. IV, p. 48].

Let A and B be dual to each other, then a topology in A is said *compatible* with this duality, when, with respect to this topology, A is a locally convex Hausdorff space and B is the set of all continuous linear functionals on A [5], Chap. IV, p. 67]. Especially, the weakest of these topologies is called the *weak topology* and is denoted by $\sigma(A, B)$. Put

$$W(b_i, i=1, 2, \dots, n; \varepsilon) = \{a \in A; |b_i(a)| < \varepsilon, i=1, 2, \dots, n\}$$

for every $\varepsilon > 0$ and every finite set of $b_i \in B$ ($i=1, 2, \dots, n$). These $W(b_i, \varepsilon)$ form a fundamental system of neighbourhoods of $o \in A$ in $\sigma(A, B)$ [5], Chap. IV, p. 50].

It is clear that $\mathfrak{A}_{sa}$ and $\mathfrak{F}_r(\mathfrak{A}$ and $\mathfrak{F})$ are dual to each other, and so it is natural to use a topology which is compatible with this duality. In particular, let us consider the weak topology $\sigma(\mathfrak{A}_{sa}, \mathfrak{F}_r)$. We can easily show that fundamental neighbourhoods of $a_0 \in \mathfrak{A}_{sa}$ are sets of elements such that $|f_i(a) - f_i(a_0)| < \varepsilon$, $f_i \in \mathfrak{F}_0$, $i=1, 2, \dots, n$. From the physical point of view, on the other hand, we can roughly say that two field quantities which take almost equal values in a finite number of states are near in some sense, namely if $f_i(a_1) \doteq f_i(a_2)$, $i=1, 2, \dots, n$, then $a_1 \doteq a_2$. These two concepts, i.e., the fundamental neighbourhoods in $\sigma(\mathfrak{A}_{sa}, \mathfrak{F}_r)$ and the nearness from the physical point of view, are in accordance with each other. Therefore it will be natural to take the topology $\sigma(\mathfrak{A}_{sa}, \mathfrak{F}_r)$ for $\mathfrak{A}_{sa}$ and similarly $\sigma(\mathfrak{A}, \mathfrak{F})$ for $\mathfrak{A}$.

Of course, $a+b$ and αa are continuous functions of (a, b) and (α, a) respectively. Furthermore

Lemma 2.2. *The mapping $a \rightarrow a^*$ from $\mathfrak{A}$ to $\mathfrak{A}$ is continuous with respect to $\sigma(\mathfrak{A}, \mathfrak{F})$, and $\mathfrak{A}_{sa}$ is a closed subset of $\mathfrak{A}$. The topology which is induced on $\mathfrak{A}_{sa}$ by $\sigma(\mathfrak{A}, \mathfrak{F})$ is equivalent to $\sigma(\mathfrak{A}_{sa}, \mathfrak{F}_r)$.*

Proof. $\mathfrak{F}$ is generated by $\mathfrak{F}_r$, and if $f \in \mathfrak{F}_r$, then $f(a^*) = f(a)$. Thus the mapping $a \rightarrow a^*$ is continuous in $\sigma(\mathfrak{A}, \mathfrak{F})$. Let J be a directed set and $\lim a_i = a$ ($i \in J$), then $\lim a_i^* = a^*$, and as $\mathfrak{A}$ is a Hausdorff space $a_i = a_i^*$ ($i \in J$) imply $a = a^*$. This shows that $\mathfrak{A}_{sa}$ is a closed subset of $\mathfrak{A}$. The remainder of this lemma is obvious. Q.E.D.

It is natural to assume that any product ab of two elements of $\mathfrak{A}$ is continuous in some sense, and since the requirement of the continuity with respect to both quantities seems too restrictive, we shall assume that ab is separately continuous in some topology. If a mapping from $\mathfrak{A}$ to $\mathfrak{A}$ is continuous with respect to any topology which is compatible with the duality of $\mathfrak{A}$ and $\mathfrak{F}$, it is continuous also with respect to $\sigma(\mathfrak{A}, \mathfrak{F})$ [5], Chap. IV, p. 103]. Therefore, the following is the weakest of similar assumptions, and this fact may be considered as another advantage of taking the topology $\sigma(\mathfrak{A}, \mathfrak{F})$.

Assumption 3. *The mapping $a \rightarrow ab$ with fixed b is continuous with respect to $\sigma(\mathfrak{A}, \mathfrak{F})$ for all $b \in \mathfrak{A}$.*

Lemma 2.3. *The mapping $b \rightarrow ab$ with fixed a is continuous with respect to $\sigma(\mathfrak{A}, \mathfrak{F})$ for all $a \in \mathfrak{A}$, namely ab is separately continuous.*

Proof. Let T_1 be a mapping $b \rightarrow b^*$, and T_2 be $b^* \rightarrow b^*a^*$. As these mappings are continuous, the mapping $(T_1 \cdot T_2 \cdot T_1)b = ab$ is continuous. Q.E.D.

Thus we may say that the topology $\sigma(\mathfrak{A}, \mathfrak{F})$ is compatible with the algebraic structure of $\mathfrak{A}$.

§ 3. Real commutative subalgebra

The fundamental postulate in § 2 is that every self-adjoint field quantity has a definite mean value in each state, but an *order relation* in $\mathfrak{A}_{sa}$, in other words a *comparison* of any two field quantities, will be a more fundamental problem. For example, let us consider the measurement of the length L of a rod, and let the length of a standard rod be L_0 . Then the measurement is reduced to the comparisons between L and nL_0 , $n=1, 2, \dots$. In general, the measurement of any physical quantity can be reduced to the comparisons of this quantity with standard quantities which we may call scales. As an idealized scale must have a constant value in any state, it will have a close connection with ae , $a \in \mathfrak{R}$, and so we shall be able to *compare* any physical quantity $a \in \mathfrak{A}_{sa}$ with ae . In this section we define the precise mathematical meaning of the *comparison*, and study the *order relation* in $\mathfrak{A}_{sa}$.

Let A be a real vector space in which an order relation $\succsim$ is defined. A is called an *ordered vector space* [6], pp. 1, 238], if

- (i) $a \succsim b$ implies $a + c \succsim b + c$,
- (ii) $\alpha \geq 0$ and $a \succsim 0$ imply $\alpha a \succsim 0$.

When we compare any element $a \in \mathfrak{A}_{sa}$ with $b \in \mathfrak{A}_{sa}$, it is natural to say that a is greater than or equal to b if $f(a) \succsim f(b)$ for all $f \in \mathfrak{F}$, and we write it $a \succsim b$. Then it is easy to show that $\mathfrak{A}_{sa}$ is an ordered vector space, and that the set $\mathfrak{P}$ of all elements $a \succsim 0$ is a closed convex cone in $\mathfrak{A}_{sa}$ with respect to $\sigma(\mathfrak{A}_{sa}, \mathfrak{F})$ [5], Chap. II, p. 49]. Further let

$$\mathfrak{P}_0 = \{a; a = \sum_{i=1}^n \alpha_i a_i^2, \alpha_i \geq 0, a_i \in \mathfrak{A}_{sa}, n=1, 2, \dots\},$$

then we have

Lemma 3.1. *Let the closure of $\mathfrak{P}_0$ be $\overline{\mathfrak{P}}_0$, then $\overline{\mathfrak{P}}_0 = \mathfrak{P}$.*

Proof. As $\mathfrak{P}$ is closed, it is clear that $\mathfrak{P}_0 \subset \mathfrak{P}$. If $\mathfrak{P}_0 \neq \mathfrak{P}$, then there is an element $a \in \mathfrak{P}$ which does not belong to $\mathfrak{P}_0$. Since $\mathfrak{P}_0$ is closed convex, there is a functional $f \in \mathfrak{F}$, such that $f(a) < f(b)$ for all $b \in \mathfrak{P}_0$ [5], Chap. II, p. 73]. As $0 \in \mathfrak{P}_0$, $f(a) < 0$. On the other hand, $b \in \mathfrak{P}_0$ implies $\alpha b \in \mathfrak{P}_0$ for all $\alpha > 0$, and then $f(b) > 0$ for all $b \in \mathfrak{P}_0$. Therefore $(1/f(c))f \in \mathfrak{F}$ and $f(a) < 0$. This is a contradiction. Q.E.D.

As $a \succsim b$ means that $f(a) \succsim f(b)$ for all $f \in \mathfrak{F}$, this order relation seems to be very suitable to $\mathfrak{A}_{sa}$ from the physical point of view, and so we expect that in some sense the order relation is compatible with the structures of $\mathfrak{A}_{sa}$ and $\mathfrak{A}$. The structures of $\mathfrak{A}_{sa}$ and $\mathfrak{A}$ can be considered from two points of view, namely

- i) the algebraic structure,
- ii) the topological structure.

i) As $\mathfrak{A}_{\varepsilon a}$ is an ordered vector space, it is clear that the order relation is compatible with the structure of $\mathfrak{A}_{\varepsilon a}$ as a vector space [5), Chap. II, p. 48]. Therefore, if $a, b \geq 0$ imply $ab \leq 0$, the order relation may be said to be compatible with the algebraic structure [7), p. 71]. However, we cannot assume this property in $\mathfrak{A}_{\varepsilon a}$, because $a, b \in \mathfrak{A}_{\varepsilon a}$ does not imply $ab \in \mathfrak{A}_{\varepsilon a}$ in general. A necessary and sufficient condition that $ab \in \mathfrak{A}_{\varepsilon a}$ for $a, b \in \mathfrak{A}_{\varepsilon a}$ is that $ab = ba$. From these considerations we assume

Assumption 4. If $ab = ba$ and $a, b \geq 0$, then $ab \geq 0$.

Therefore, to study an order relation compatible with an algebraic structure it is necessary to take a commutative subalgebra whose elements are all self-adjoint, and we call such a subalgebra a *real commutative subalgebra*. In quantum mechanics such a subalgebra plays a very essential role. Namely, a maximal real commutative subalgebra is a *complete set of commuting observables*, and in a very rough sense we can represent them simultaneously by diagonal matrices, and the simultaneous eigenstates of these observables form a complete orthonormal set in the Hilbert space.

Let $\mathfrak{m}$ be any maximal real commutative subalgebra of $\mathfrak{A}$. It is clear that $\mathfrak{m}$ is closed and $e \in \mathfrak{m}$. Put

$$\mathfrak{m}^0 = \{f; f \in \mathfrak{F}_r, f(a) = 0, a \in \mathfrak{m}\},$$

and $\mathfrak{F}_m = \mathfrak{F}_r / \mathfrak{m}^0$. Let $\bar{f} \in \mathfrak{F}_m$ be the class to which f belongs, and $\bar{f}(a) = f(a)$. Then $\bar{f}$ is a linear functional on $\mathfrak{m}$, $\mathfrak{m}$ and $\mathfrak{F}_m$ are dual to each other, and $\sigma(\mathfrak{m}, \mathfrak{F}_m)$ is equivalent to the topology which is induced on $\mathfrak{m}$ by $\sigma(\mathfrak{A}_{\varepsilon a}, \mathfrak{F}_r)$ [5), Chap. IV, p. 54]. Now, $\mathfrak{m}$ is an ordered vector space with respect to the above defined order relation, $\mathfrak{P}_m = \mathfrak{P} \cap \mathfrak{m}$ is a closed convex cone and $\mathfrak{P}_m = \{a \in \mathfrak{m}; a \geq 0\}$. Put

$$\mathfrak{S}_m = \{\bar{f}; f \in \mathfrak{S}, \bar{f} \in \mathfrak{F}_m\}.$$

In order to study the properties of $\mathfrak{m}$ we can use $\mathfrak{S}_m$ instead of $\mathfrak{S}$.

- ii) Next, the order relation is to be compatible with the topological structure of $\mathfrak{m}$. For that purpose, we define *order-convergences* as follows.

Let $a_i \downarrow 0$, $i, \kappa \in J$ (directed set) mean that $i \leq \kappa$ implies $a_i \geq a_\kappa$, and that the greatest lower bound of $\{a_i\}$ is 0, that is $\bigwedge \{a_i; i \in J\} = 0$. If $(a - a_i) \downarrow 0$ or $(a_i - a) \downarrow 0$, we write $a_i \uparrow a$ or $a_i \downarrow a$ respectively, and we say that $\{a_i\}$ *order-converges* to a [6), p. 40].

As $\bar{f} \in \mathfrak{F}_m$ is continuous in any topology which is compatible with the duality in $\mathfrak{m}$ and $\mathfrak{F}_m$, we may say that the order relation is compatible with the topological structure of $\mathfrak{m}$ if and only if $a_i \downarrow 0$ imply $\bar{f}(a_i) \rightarrow 0$. Thus we assume

Assumption 5. If $a_i \downarrow 0$, then $\bar{f}(a_i) \rightarrow 0$ for all $\bar{f} \in \mathfrak{F}_m$.

From this we can easily show that, if $a_i \uparrow a$ or $a_i \downarrow a$, $a_i \rightarrow a$ in $\sigma(\mathfrak{m}, \mathfrak{F}_m)$. Conversely, if $\{a_i\}$, $a_i \geq 0$ is a directed set of points such that $i \leq \kappa$ implies $a_i \geq a_\kappa$, and $a_i \rightarrow 0$ in $\sigma(\mathfrak{m}, \mathfrak{F}_m)$ then $a_i \downarrow 0$. From the above considerations we may say that the *order relation in $\mathfrak{m}$ is compatible with the structure of it*. Now we must study $\mathfrak{m}$ in detail.

Let A be an ordered vector space. If for any $a, b \in A$ there is a least upper bound $a \cup b$, we call A a *vector lattice*, and if every bounded subset has a least upper bound

(l.u.b.) and a greatest lower bound (g.l.b.), we call it a *complete vector lattice* [6], p. 238]. An ordered vector space A is called *Archimedean* if and only if $a \geq nb$, $n=1, 2, \dots$, imply $b \leq 0$ [6], p. 225].

Lemma 3.2. m is Archimedean.

Proof. If $a \geq nb$, $n=1, 2, \dots$, then $f(a) \geq nf(b)$, for all $\bar{f} \in \mathfrak{Z}_m$, and then $\bar{f}(b) \leq 0$ and $b \leq 0$. Q.E.D.

If an ordered vector space A is Archimedean, and if, for any two elements $a, b \in A$ there exists an element c such that $a, b \leq c$, then a *completion by cuts* of A is a complete vector lattice $\bar{A}$ [6], p. 58; 7), p. 68]. Since

$$a, b \leq (1/2)(e+a)^2 + (1/2)(e+b)^2 \in m$$

for any two $a, b \in m$, we get

Theorem 1. Let the completion by cuts of m be $\bar{m}$, then $\bar{m}$ is a complete vector lattice and m is embedded in $\bar{m}$, so that all g.l.b. and l.u.b. existing in m are preserved.

Thus $a \in m$ can be divided uniquely in $\bar{m}$ as follows:

$$a = a^+ - a^-, \quad a^+, a^- \geq 0, \quad a^+ = a \cup 0.$$

In the usual theory the positive and negative parts of any field quantity are also field quantities in a rough sense. Therefore we also assume that a and a^+ be field quantities in the following sense.

Assumption 6. If $a^+ \neq 0$, $a \in m$, then there is an element $a' \in m$ such that $a^+ \geq a' > 0$.

At first sight this assumption will be seen to be short to express that a^+ is a physical quantity in some sense. But Lemma 3.4 will show that a^+ gives a definite expectation value $\bar{f}(a^+)$ in any $\bar{f} \in \mathfrak{Z}_m$, and that, if $f(a^+) = 0$ for all $\bar{f} \in \mathfrak{Z}_m$, then $a^+ = 0$. Thus we shall be able to say that a^+ is a field quantity in this sense. From Assumption 6, it is clear that for any $a > 0$, $a \in \bar{m}$, there exists $a' \in m$ such that $a \geq a' > 0$.

Lemma 3.3. For any $a \in \bar{m}$, there exists a directed set of points $\{a_i\}$ such that $a_i \in m$ and $a_i \uparrow a$, and $\{a'_i\}$ such that $a'_i \in m$ and $a'_i \downarrow a$.

Proof. Let $a \geq 0$. If $a = 0$, the lemma is obvious. If $a > 0$, there exists $a_1 \in m$ such that $a \geq a_1 > 0$, and $a - a_1 \geq 0$. If $a - a_1 = 0$, the lemma is obvious. If $a - a_1 > 0$, there exists $b_1 \in m$ such that $a - a_1 \geq b_1 > 0$, and $a - (a_1 + b_1) \geq 0$. Put $a_2 = a_1 + b_1$, then $a_2 \in m$ and $a \geq a_2 > a_1 > 0$. Repeating such procedures transfinitely, we can get a desired directed set of points $\{a_i\}$. For any $a \in m$, there exists $b \in m$ such that $a \leq b$, and let $c_i \uparrow (a - b)$, then putting $a'_i = b + c_i$, we can show $a'_i \downarrow a$. Q.E.D.

Lemma 3.4. Defining $f(a)$ for all $\bar{f} \in \mathfrak{Z}_m$ and $a \in m$ properly, we can make m and $\mathfrak{Z}_m$ dual to each other.

Proof. For any $\bar{f} \in \mathfrak{Z}_m$ and $a \in \bar{m}$, we define

$$\bar{f}_{\sup}(a) = \sup \{ \bar{f}(a'); a' \leq a, a' \in m \},$$

and

$$\bar{f}_{\inf}(a) = \inf \{ \bar{f}(a'); a' \geq a, a' \in m \}.$$

There is an element $b \in m$ such that $b \geq a$, then $f(b) \geq f(a')$, and it is clear that $\bar{f}_{\sup}(a)$

exists. In the same manner, we can show that $\bar{f}_{\inf}(a)$ exists. Let $b_i \uparrow a$, $b_i \in \mathfrak{m}$ and $c_\kappa \downarrow a$, $c_\kappa \in \mathfrak{m}$, and put $d_{(\kappa, i)} = (c_\kappa - a) + (a - b_i) = c_\kappa - b_i$. If we put $(\kappa, i) \leq (\kappa', i')$ when and only when $\kappa \leq \kappa'$ and $i \leq i'$, then $\{(\kappa, i)\}$ is a directed set and $d_{(\kappa, i)} \downarrow 0$. Thus $\bar{f}(d_{(\kappa, i)}) \rightarrow 0$, namely $\{\bar{f}(c_\kappa) - \bar{f}(b_i)\} \rightarrow 0$, and it follows $\wedge \bar{f}(c_\kappa) = \vee \bar{f}(b_i)$ and $\bar{f}_{\sup}(a) = \bar{f}_{\inf}(a)$. Now we define that $\bar{f}(a) = \bar{f}_{\sup}(a) = \bar{f}_{\inf}(a)$. From this we can easily show that $\bar{f}$ is a linear functional on $\bar{\mathfrak{m}}$. Further we can show that for any $\bar{f}_1, \bar{f}_2 \in \mathfrak{S}_{\bar{\mathfrak{m}}}$ and $\alpha, \beta \geq 0$, $\alpha + \beta = 1$,

$$(\alpha \bar{f}_1 + \beta \bar{f}_2)(a) = \alpha \bar{f}_1(a) + \beta \bar{f}_2(a).$$

Let $\bar{f} \in \mathfrak{S}_{\bar{\mathfrak{m}}}$ be $\bar{f} = \alpha \bar{f}_1 - \beta \bar{f}_2 = \alpha' \bar{f}_1' - \beta' \bar{f}_2'$, where $\alpha, \beta, \alpha', \beta' \geq 0$, and $\bar{f}_1, \bar{f}_2, \bar{f}_1', \bar{f}_2' \in \mathfrak{S}_{\bar{\mathfrak{m}}}$, then $\alpha \bar{f}_1 + \beta' \bar{f}_2' = \alpha' \bar{f}_1' + \beta \bar{f}_2$, and $\alpha \bar{f}_1(a) + \beta' \bar{f}_2'(a) = \alpha' \bar{f}_1'(a) + \beta \bar{f}_2(a)$, namely $\alpha \bar{f}_1(a) - \beta \bar{f}_2(a) = \alpha' \bar{f}_1'(a) - \beta' \bar{f}_2'(a)$. Therefore we can uniquely define

$$\bar{f}(a) = \alpha \bar{f}_1(a) - \beta \bar{f}_2(a),$$

and $\bar{f} \in \mathfrak{S}_{\bar{\mathfrak{m}}}$ defines a linear functional on $\bar{\mathfrak{m}}$, and $a \in \bar{\mathfrak{m}}$ does on $\mathfrak{S}_{\bar{\mathfrak{m}}}$. Let $a \in \bar{\mathfrak{m}}$ and $\bar{f}(a) = 0$ for all $\bar{f} \in \mathfrak{S}_{\bar{\mathfrak{m}}}$, then there is at least one $\{a_i\}$ such that $a_i \downarrow a$, $a_i \in \mathfrak{m}$. Since $\bar{f}(a_i) \geq \bar{f}(a) = 0$, $a_i \geq 0$. Hence $a \geq 0$. In the same way we can show $a \leq 0$. This proves $a = 0$.

Q.E.D.

Lemma 3.5. We can define a product ab for all $a, b \in \bar{\mathfrak{m}}$ such that $\bar{\mathfrak{m}}$ is a commutative algebra in which $a, b \geq 0$ imply $ab \geq 0$ and $\mathfrak{m}$ is a subalgebra of $\bar{\mathfrak{m}}$.

Proof. For any $a \geq 0$, $a \in \mathfrak{m}$ and $b \in \bar{\mathfrak{m}}$, we put

$$(ab)_{\mathfrak{u}} = \vee \{ab' ; b' \leq b, b' \in \mathfrak{m}\},$$

and

$$(ab)_i = \wedge \{ab'' ; b'' \geq b, b'' \in \mathfrak{m}\}.$$

As $\bar{\mathfrak{m}}$ is complete, the existence of these two elements are clear. Let $b'_i \uparrow b$ and $b''_\kappa \downarrow b$, then $(b''_\kappa - b'_i) = b_{(\kappa, i)} \downarrow 0$. It follows $b_{(\kappa, i)} \rightarrow 0$, and $ab_{(\kappa, i)} \rightarrow 0$ by Lemma 2.3. As $a \geq 0$, this implies that $ab_{(\kappa, i)} \downarrow 0$, that is $(ab''_\kappa - ab'_i) \downarrow 0$. This shows that $(ab)_{\mathfrak{u}} = (ab)_i$, and we can define $ab = (ab)_{\mathfrak{u}} = (ab)_i$. Let $m \ni a$, $a_1, a_2 \geq 0$, and $\bar{\mathfrak{m}} \ni b$, b_1, b_2 , then it is clear that

$$(a_1 + a_2)b = a_1b + a_2b, \quad a(b_1 + b_2) = ab_1 + ab_2,$$

and $(a_1b)a_2 = a_1(ba_2)$. For any $a \in \mathfrak{m}$, $a = a_1 - a_2$ and $a_1, a_2 \geq 0$, we can define $ab = ba = a_1b - a_2b$ as in Lemma 3.4. Similarly we can define ab for any $a, b \in \bar{\mathfrak{m}}$. Let $a, b \geq 0$, $a_\kappa, b_i \in \mathfrak{m}$. If $a_\kappa \downarrow a$, $b_i \uparrow b$, we have

$$\bigwedge_{\kappa} a_\kappa b - \bigvee_i ab_i = \bigwedge_{\kappa} [a_\kappa(b - b_i) + (a_\kappa - a)b_i] \geq \bigwedge_{\kappa} a_\kappa(b - b_i) + \bigwedge_{\kappa} (a_\kappa - a)b_i = 0,$$

and if $a'_\kappa \uparrow a$, $b'_i \downarrow b$,

$$\bigvee_{\kappa} a'_\kappa b - \bigwedge_i ab'_i = \bigvee_{\kappa} [a'_\kappa(b - b'_i) + (a'_\kappa - a)b'_i] \leq \bigvee_{\kappa} a'_\kappa(b - b'_i) + \bigvee_{\kappa} (a'_\kappa - a)b'_i = 0.$$

As $\bigwedge_{\kappa} a_\kappa b = \bigvee_{\kappa} a'_\kappa b$ and $\bigvee_i ab_i = \bigwedge_i ab'_i$, this proves that the above definition of ab is unique. If $a, b, c \geq 0$, then

$$(ab)c = (\bigwedge_{\kappa} a_{\kappa} b)c = \bigwedge_{\kappa} [(a_{\kappa} b)c] = \bigwedge_{\kappa} \bigwedge_{\epsilon} [(a_{\kappa} b)c_{\epsilon}] = \bigwedge_{\kappa} \bigwedge_{\epsilon} [a_{\kappa}(bc_{\epsilon})] = \bigwedge_{\kappa} a_{\kappa}(bc) = a(bc).$$

The remainder of the lemma can be shown easily.

Q.E.D.

In a vector lattice A an element a_0 is called a *unit* if and only if $a_0 \cap b = 0$ imply $b = 0$ for all $b \geq 0$, and for convenience' sake we call this L-unit, and a unit in an algebra A-unit. In the beginning of this section we have pointed out that we would be able to compare any physical quantity $a \in \mathfrak{A}_m$ with ae . Now we are in a position to set up an assumption which will realize this proposition. Though $\mathfrak{m}$ is not necessarily a vector lattice, this assumption will mean that e is something like an L-unit, namely we assume

Assumption 7. For any $a > 0$, $a \in \mathfrak{m}$, there is an element $a' > 0$, $a' \in \mathfrak{m}$ such that $a \geq a'$ and $e \geq a'$.

From Assumptions 6 and 7, we can easily show that e is an L-unit of $\overline{\mathfrak{m}}$. Let an element $a \in \mathfrak{m}$ satisfy the condition that there is a positive number α such that $a \geq f(\alpha) \geq -\alpha$ for all $f \in \mathfrak{Z}_m$, namely $ae \geq a \geq -ae$, then we call it *bounded*. Assumption 7 means that for any $a > 0$, $a \in \mathfrak{m}$, there exists a bounded element $a' \in \mathfrak{m}$ such that $a \geq a' > 0$, and we can show as in Lemma 3.3 that there is a sequence of bounded elements $a_i \in \mathfrak{m}$ such that $a_i \uparrow a$. Therefore Assumption 7 may be interpreted as that any element $a \in \mathfrak{m}$ can be approximated in some sense by a sequence of bounded elements.

When a vector lattice A is a commutative algebra such that A-unit is L-unit and that $a, b \geq 0$ imply $ab \geq 0$, then A is called a *lattice ordered ring* [7], p. 69, and

Theorem 2. $\overline{\mathfrak{m}}$ is a lattice ordered ring.

In [7], Chap. IV], it is shown that, on a certain topological space Ω , the set $\mathfrak{Q}$ of all continuous functions which are finite almost everywhere can be considered as a complete vector lattice, and that $\overline{\mathfrak{m}}$ and $\mathfrak{m}$ can be represented by an ideal $\mathfrak{Q}_m$ of $\mathfrak{Q}$ and a subset $\mathfrak{Q}_m$ of $\mathfrak{Q}_m$ respectively. It is further shown that if F_a be a function corresponding to a , then $F_a F_b = F_{ab}$ and $F_e = 1$. From this we can easily show that $a^+ = 0$ implies $a = 0$, and that $a = a^+ - a^-$ imply $a^+ a^- = 0$.

Lemma 3.6. For any $a \geq 0$, $a \in \overline{\mathfrak{m}}$, there exists $\{b_i\}$, $b_i \in \mathfrak{m}$, such that $b_i \geq 0$ and $(b_i)^2 \uparrow a$.

Proof. F_a is continuous, and so $(F_a)^{1/2} \geq 0$ is also continuous. As $F_e + F_a \geq 2(F_a)^{1/2} \geq 0$, and $\mathfrak{Q}_m$ is an ideal, $(F_a)^{1/2} \in \mathfrak{Q}_m$. Let $a^{1/2}$ be the element corresponding to $(F_a)^{1/2}$, then there exist $b_i \in \mathfrak{m}$ such that $b_i \uparrow a^{1/2}$, and $(b_i)^2 \uparrow a$. Q.E.D.

§ 4. Representation of $\mathfrak{A}$

In the last section we have studied the various properties of the real commutative subalgebras. Now, using these results, we can show that $\mathfrak{A}$ can be represented by an operator algebra in a Hilbert space. We begin with the following theorem.

Theorem 3. For any $a \in \mathfrak{A}$, $a^* a \geq 0$, and $a^* a = 0$ implies $a = 0$.

Proof. We first show that, if $a^* a = -b$ and $b \geq 0$, then $b = 0$. Let $\mathfrak{m}$ be a maximal real commutative subalgebra to which b belongs, then from Lemma 3.6, there exists $\{c_i\}$ such that $(c_i)^2 \geq b$, $c_i \geq 0$, and $c_i \in \mathfrak{m}$. Let $ac_i = u_i + iv_i$, $u_i, v_i \in \mathfrak{A}_{m,i}$, then

$$(ac_i)(ac_i)^* + (ac_i)^*(ac_i) = 2[(v_i)^2 + (v_i)^2] \geq 0.$$

On the other hand

$$(ac_i)^*(ac_i) = c_i a^* ac_i = - (c_i)^2 b \leq 0.$$

Hence

$$(ac_i)(ac_i)^* = a(c_i)^2 a^* \geq 0.$$

and as $\mathfrak{A}$ is closed, $aba^* \geq 0$. Since

$$(aa^*)^2 + aba^* = aa^*aa^* + aba^* = -aba^* + aba^* = 0,$$

$(aa^*)^2, aba^* \geq 0$ imply $(aa^*)^2 = 0, aa^* = 0$, then $a^*aa^*a = 0, a^*a = 0$. Next, let a be any element of $\mathfrak{A}$, and $\mathfrak{m}$ be any maximal real commutative subalgebra to which a^*a belongs, and let

$$a^*a = u^+ - u^-, \quad u^+ u^- = 0, \quad u^+, u^- \geq 0.$$

If $u^- \neq 0$, from Lemma 3.6 there exists $v > 0$ such that $u \geq v^2 > 0, v \in \mathfrak{m}$, and $u^+ v^2 = 0$. Therefore $u^- v^2 \in \mathfrak{m}$ and $va^*av = -v^2 u^-$, namely $(av)^*(av) = -v^2 u^-$. Thus $v^2 u^- = 0$, this is a contradiction, and accordingly $u^- = 0, a^*a \geq 0$. The remainder of the theorem can be easily shown. Let $a = u + iv, u, v \in \mathfrak{A}_{\text{sa}}$. As $a^*a = 0, aa^*aa^* = (aa^*)^2 = 0$, namely $aa^* = 0$. Thus $a^*a + aa^* = 2(u^2 + v^2) = 0$, and $u = v = 0$. Q.E.D.

If we assumed $a^*a \geq 0$ from the outset, we could extremely simplify the argument, but since the physical meaning of *adjoint* is not clear we have not assumed this. On the contrary, the Assumptions in § 3, from which we can prove Theorem 3, refer only to the self-adjoint elements, and their physical meanings have been explained in § 3. This is the reason why we have followed such a complicated course.

Lemma 4.1. Put for any $f \in \mathfrak{S}$

$$\mathfrak{Y}_f = \{a; f(a^*a) = 0\},$$

then $\mathfrak{Y}_f$ is a closed left-ideal of $\mathfrak{A}$, and

$$\mathfrak{Y}_f = \{a; f(\mathfrak{A}a) = 0\}.$$

Proof. Let $f(a^*a) = 0$, and $g(b) = f(a^*ba)$. $g(b)$ is a real linear functional on $\mathfrak{A}_{\text{sa}}$, and from Theorem 3 $g(c^2) = f((ca)^*(ca)) \geq 0$ for any $c \in \mathfrak{A}_{\text{sa}}$, and $g(e) = f(a^*a) = 0$. It follows from Lemma 2.1 that $g(b) = f(a^*ba) = 0$. Namely for any $c \in \mathfrak{A}$, $f((ca)^*(ca)) = f(a^*c^*ca) = 0$, and then $\mathfrak{A}\mathfrak{Y}_f \subseteq \mathfrak{Y}_f$. For any $a \in \mathfrak{Y}_f$ and $\alpha \in \mathfrak{R}$,

$$f(e) - \alpha f(a + a^*) = f((e - \alpha a)^*(e - \alpha a)) \geq 0,$$

therefore $f(a + a^*) = 0$. In the same way, we have $f(ia - ia^*) = 0$, and hence $f(a) = f(a^*) = 0$. Hence for all $a \in \mathfrak{Y}_f$, $f(\mathfrak{A}a) = f(a^*\mathfrak{A}) = 0$. On the contrary, $f(\mathfrak{A}a) = 0$ implies $a \in \mathfrak{Y}_f$, then it is clear that, if $a, b \in \mathfrak{Y}_f$, $a + b \in \mathfrak{Y}_f$ and $\mathfrak{Y}_f$ is a subalgebra. If $a_i \in \mathfrak{Y}_f$ and $a_i \rightarrow a$, $f(\mathfrak{A}a_i) = 0$ and then $f(\mathfrak{A}a) = 0$. That is $a \in \mathfrak{Y}_f$, and $\mathfrak{Y}_f$ is closed. Q.E.D.

Theorem 4. For any $f \in \mathfrak{S}$, there is defined a Hilbert space $\mathfrak{H}_f$, and $\mathfrak{A}/\mathfrak{Y}_f$ is a subset which is everywhere dense in $\mathfrak{H}_f$. There is an operator algebra in $\mathfrak{H}_f$, which is homomorphic to $\mathfrak{A}$,

Proof. Let $\tilde{a}, \tilde{b}, \dots$ be elements of a linear space $\mathfrak{A}/\mathfrak{I}_f$. For any element $b \in \mathfrak{A}$, we can define a linear operator b_f in $\mathfrak{A}/\mathfrak{I}_f$ by $b_f \tilde{a} = \tilde{b}a$, and let the set of these operators be $\mathfrak{A}_f$. It is clear that $b \rightarrow b_f$ is a homomorphism of $\mathfrak{A}$ onto $\mathfrak{A}_f$. From Lemma 4.1 $f((b^* + \mathfrak{I}_f^*)(a + \mathfrak{I}_f)) = f(b^*a)$, and we can define an inner product in $\mathfrak{A}/\mathfrak{I}_f$ by $(\tilde{b}, \tilde{a}) = f(b^*a)$, and it is easy to show that this is a proper inner product [8], p. 3. Let $\|\tilde{a}\| = [(\tilde{a}, \tilde{a})_f]^{1/2}$ be a norm of $\tilde{a}$, and let the completion of $\mathfrak{A}/\mathfrak{I}_f$ be $\mathfrak{H}_f$, then $\mathfrak{H}_f$ is a Hilbert space. $\mathfrak{A}_f$ is a set of operators in $\mathfrak{H}_f$, and the domains of these operators are everywhere dense in $\mathfrak{H}_f$, namely $\mathfrak{A}/\mathfrak{I}_f$. Since

$$(\tilde{b}, a_f \tilde{c})_f = f(b^*ac) = f((a^*b)^*c) = (a^* \tilde{b}, \tilde{c})_f = ((a^*)_f \tilde{b}, \tilde{c})_f$$

a_f and $(a^*)_f$ are adjoint to each other [8], p. 41].

Q.E.D.

Theorem 5. $\mathfrak{A}$ is isomorphic to an operator algebra in a Hilbert space $\mathfrak{H}$.

Proof. Let $\mathfrak{H} = \bigoplus \{\mathfrak{H}_f; f \in \mathfrak{Z}\}$ be the external Hilbertian direct sum of $\{\mathfrak{H}_f; f \in \mathfrak{Z}\}$ [5], Chap. V, p. 146]. For any $a \in \mathfrak{A}$, let $a_{\mathfrak{H}}$ be the operator in $\mathfrak{H}$ which can be identified with a_f in each $\mathfrak{H}_f$, and whose domain $\mathfrak{D}$ is the direct sum of $\mathfrak{A}/\mathfrak{I}_f$ with the condition that only finite number of components are not 0. Put the set of all these operators $\mathfrak{A}_{\mathfrak{H}}$, then it is clear that $\mathfrak{A}_{\mathfrak{H}}$ is homomorphic to $\mathfrak{A}$. Let $a_{\mathfrak{H}} = o$, then for all $f \in \mathfrak{Z}$ and $\tilde{b} \in \mathfrak{H}_f$, $a_f \tilde{b} = o$ in $\mathfrak{H}_f$. Putting $b = e$, we get $f(a^*a) = o$. This shows that $a^*a = o$, $a = o$.

Q.E.D.

Lemma 4.2. Put $g(b) = (\tilde{a}, b_f \tilde{a})_f$ for any $\tilde{a} \in \mathfrak{A}/\mathfrak{I}_f$, $\tilde{a} \neq \tilde{o}$, then $(1/g(e))g(b) \in \mathfrak{Z}$.

Proof. From the continuity of the product, it follows that $g(b)$ is a linear continuous functional on $\mathfrak{A}_{\mathfrak{H}}$, that is $g(b) \in \mathfrak{K}_{\mathfrak{H}}$, and then the lemma is obvious. Q.E.D.

In Theorem 5, $\mathfrak{H}$ is not necessarily separable, but in quantum mechanics the state vectors form a separable Hilbert space, and if it is not separable there will occur many troubles. Therefore we expect that by appropriate physical assumptions $\mathfrak{H}$ can be made separable. In the following, we make an additional assumption from such points of view, but we may say that it is too artificial and that its physical meaning is not sufficiently clear. The main purpose of the following discussion is to show that the separability of $\mathfrak{H}$ is closely related to the physical viewpoint. Therefore, in the following sections, we do not use the Assumption 8) but the separability of $\mathfrak{H}$.

We can make only an enumerable number of experiments, and $f(a)$ can be determined by these experiments. Thus the number of $f(a)$ which we can determine by experiments is at most enumerable. Hence we may assume that there is an enumerable set $\mathfrak{A}_e$ which is everywhere dense in $\mathfrak{A}$ in a sense. Considering that $\mathfrak{A}$ is not only a vector space but an algebra, we assume

Assumption 8. i) There is an enumerable set $\mathfrak{A}_e$ of elements of $\mathfrak{A}$ such that for any $a \in \mathfrak{A}$ there are $a_n \in \mathfrak{A}_e$, $n = 1, 2, \dots$, which satisfy the conditions that $a_n \rightarrow a$ and $a_n^* a_n \rightarrow a^* a$ in $\sigma(\mathfrak{A}, \mathfrak{I})$.

On the same ground we assume also

ii) There is an enumerable set $\mathfrak{Z}_e$ of elements of $\mathfrak{Z}$ such that $f_i(a) = 0$ for all $f_i \in \mathfrak{Z}_e$ imply $f(a) = 0$ for all $f \in \mathfrak{Z}$.

Lemma 4.3. $\mathfrak{H}_f$ is separable.

Proof. Let $(\mathfrak{A}/\mathfrak{H}_f)_e$ be the enumerable set of classes each of which contains at least one element of $\mathfrak{A}_e$. From Assumption 8, i) it is easy to show that for any $\tilde{a} \in \mathfrak{A}/\mathfrak{H}_f$, there are $\tilde{a}_n \in (\mathfrak{A}/\mathfrak{H}_f)_e$, $n=1, 2, \dots$, such that $(\tilde{a}_n, \tilde{b})_f \rightarrow (\tilde{a}, \tilde{b})_f$ for all $\tilde{b} \in (\mathfrak{A}/\mathfrak{H}_f)$ and that $\|\tilde{a}_n\| \rightarrow \|\tilde{a}\|$. As $\mathfrak{A}/\mathfrak{H}_f$ is everywhere dense in $\mathfrak{H}_f$, this shows that $\tilde{a}_n \rightarrow \tilde{a}$ in the strong topology in $\mathfrak{H}_f$, namely $\|\tilde{a} - \tilde{a}_n\| \rightarrow 0$. Thus $(\mathfrak{A}/\mathfrak{H}_f)_e$ is everywhere dense in $\mathfrak{H}_f$.
Q.E.D.

From Lemma 4.3 and Assumption 8, ii) we can easily show, like Theorem 5, that

Theorem 6. Let $\mathfrak{H} = \bigoplus \{\mathfrak{H}_f; f \in \mathfrak{S}_e\}$ be the external Hilbertian direct sum of $\{\mathfrak{H}_f; f \in \mathfrak{S}_e\}$, then $\mathfrak{H}$ is separable, and $\mathfrak{A}$ is isomorphic to an operator algebra in $\mathfrak{H}$.

§ 5. Representation of states

In the last section we have shown that $\mathfrak{A}$ can be represented isomorphically as an operator algebra $\mathfrak{A}_{\mathfrak{H}}$ in a separable Hilbert space $\mathfrak{H}$. Now, in this section, we shall study more precisely the relations between $\mathfrak{A}$ and $\mathfrak{A}_{\mathfrak{H}}$ and especially the representation of states.

Let $a_{\mathfrak{H}}$ be the operator in $\mathfrak{H}$ which corresponds to $a \in \mathfrak{A}$, then it is clear that the domain $\mathfrak{H}_0$ of $a_{\mathfrak{H}}$ is everywhere dense in $\mathfrak{H}$. ($\mathfrak{H}_0$ is defined as in the proof of Theorem 5.)

Lemma 5.1. If $a = a^*$, $a_{\mathfrak{H}}$ is symmetric [8], p. 49].

Proof. It is clear from the definition of a symmetric transformation in $\mathfrak{H}$.

Q.E.D.

Lemma 5.2. If $a \in \mathfrak{A}_{sa}$ is bounded, then there is a unique self-adjoint and bounded extension $\bar{a}_{\mathfrak{H}}$ of $a_{\mathfrak{H}}$. If $a \geq 0$, $a \in \mathfrak{A}_{sa}$, then there is a self-adjoint extension $\bar{a}_{\mathfrak{H}}$ of $a_{\mathfrak{H}}$, and the spectrum of $\bar{a}_{\mathfrak{H}}$ is non-negative.

Proof. From Lemma 4.2, if $g(a) = (\tilde{b}, a\tilde{b})_f$ and $(\tilde{b}, \tilde{b})_f = 1$, $g \in \mathfrak{S}$. Then $\alpha e \geq a \geq -\alpha e$ implies $\alpha(\psi, \psi) \geq |(\psi, a_{\mathfrak{H}}\psi)|$ for any element $\psi \in \mathfrak{H}_0$, and as $a_{\mathfrak{H}}$ is symmetric there is a unique self-adjoint and bounded extension $\bar{a}_{\mathfrak{H}}$ [8], pp. 56, 57, 388]. On the other hand, if $a \geq 0$, $(\psi, a_{\mathfrak{H}}\psi) \geq 0$ for any element $\psi \in \mathfrak{H}_0$, and the remainder of the lemma follows at once [8], pp. 188, 388].
Q.E.D.

Lemma 5.3. Let $\mathfrak{B}'$ be the set of all bounded elements of $\mathfrak{A}$, $\mathfrak{B}$ be the subalgebra of $\mathfrak{A}$ generated by $\mathfrak{B}'$, and the corresponding subalgebra of $\mathfrak{A}_{\mathfrak{H}}$ be $\mathfrak{B}_{\mathfrak{H}}$. Then any operator $a_{\mathfrak{H}} \in \mathfrak{B}_{\mathfrak{H}}$ is bounded and has a unique bounded extension $\bar{a}_{\mathfrak{H}}$ with domain $\mathfrak{H}$. Furthermore, the set of all these $\bar{a}_{\mathfrak{H}}$ forms an algebra $\mathfrak{U}_{\mathfrak{H}}$ and it is isomorphic to $\mathfrak{B}_{\mathfrak{H}}$.

Proof. If $a \in \mathfrak{B}'$, then there exists a unique bounded extension $\bar{a}_{\mathfrak{H}}$ with domain $\mathfrak{H}$ [8], p. 57]. Therefore any element of $\mathfrak{U}_{\mathfrak{H}}$, which is generated by these $\bar{a}_{\mathfrak{H}}$, is bounded with domain $\mathfrak{H}$, and then it is continuous. This implies that $\mathfrak{U}_{\mathfrak{H}}$ is isomorphic to $\mathfrak{B}_{\mathfrak{H}}$. For example, let $ab = ba$, $a_{\mathfrak{H}}b_{\mathfrak{H}} = b_{\mathfrak{H}}a_{\mathfrak{H}} \in \mathfrak{B}_{\mathfrak{H}}$. For any $\psi \in \mathfrak{H}$, there are $\psi'_n \in \mathfrak{H}_0$, $n=1, 2, \dots$, such that $\psi'_n \rightarrow \psi$ in the strong topology in $\mathfrak{H}$. As $\bar{b}_{\mathfrak{H}}\bar{a}_{\mathfrak{H}}$ and $\bar{a}_{\mathfrak{H}}\bar{b}_{\mathfrak{H}}$ are continuous, $\bar{a}_{\mathfrak{H}}\bar{b}_{\mathfrak{H}}\psi'_n \rightarrow \bar{a}_{\mathfrak{H}}\bar{b}_{\mathfrak{H}}\psi$ and $\bar{b}_{\mathfrak{H}}\bar{a}_{\mathfrak{H}}\psi'_n \rightarrow \bar{b}_{\mathfrak{H}}\bar{a}_{\mathfrak{H}}\psi$, thus $\bar{a}_{\mathfrak{H}}\bar{b}_{\mathfrak{H}}\psi = \bar{b}_{\mathfrak{H}}\bar{a}_{\mathfrak{H}}\psi$, namely $\bar{a}_{\mathfrak{H}}\bar{b}_{\mathfrak{H}} = \bar{b}_{\mathfrak{H}}\bar{a}_{\mathfrak{H}}$. Q.E.D.

As we have shown, if a is bounded, $a_{\mathfrak{H}}$ is also bounded. If $a \geq 0$, there is a self-adjoint extension $\bar{a}_{\mathfrak{H}}$, whose spectrum is non-negative. On the contrary, we do not know

whether the inverses of these propositions can be proved or not. This is due to the following fact. From Lemma 4.2, it is easy to show that if $\psi \in \mathfrak{H}$, and $(\psi, \psi) = 1$ then $f(a) = (\psi, a_{\mathfrak{H}} \psi) \in \mathfrak{Z}$. It has not been answered as yet, on the other hand, whether any state f can be represented in the form $f(a) = (\psi, a_{\mathfrak{H}} \psi)$ or by a linear combination of these forms. Thus if $f(a) \geq 0$ for all $f \in \mathfrak{Z}$, then $(\psi, a_{\mathfrak{H}} \psi) \geq 0$ for all $\psi \in \mathfrak{H}$, but the latter does not necessarily imply the former. Therefore in the following we shall study this problem.

Let $\mathfrak{m}$ be any real commutative subalgebra, $\mathfrak{m}' = \mathfrak{m} \cap \mathfrak{B}'$, $\mathfrak{m}'' = \mathfrak{m} \cap \mathfrak{B}$, and the corresponding sets of elements of $\mathfrak{L}_{\mathfrak{H}}$ be $\mathfrak{H}'_{\mathfrak{H}}$ and $\mathfrak{H}''_{\mathfrak{H}}$ respectively. Then the weak closure of $\mathfrak{H}''_{\mathfrak{H}}$ is a Neumann's Abelian ring $\mathfrak{H}''_{\mathfrak{H}}$ [9], pp. 388, 398, and it is the smallest ring containing $\mathfrak{H}'_{\mathfrak{H}}$ or $\mathfrak{H}''_{\mathfrak{H}}$, namely $\mathfrak{H}''_{\mathfrak{H}} = \mathbf{R}(\mathfrak{H}'_{\mathfrak{H}}) = \mathbf{R}(\mathfrak{H}''_{\mathfrak{H}})$. It is shown in [9], p. 401 that there is a bounded self-adjoint operator H such that $\mathfrak{H}''_{\mathfrak{H}} = \mathbf{R}(H)$. In other words, any element of $\mathfrak{H}''_{\mathfrak{H}}$ can be represented by a bounded H -measurable function $F(\lambda)$ as $F(H)$, whereas any such operator $F(H)$ belongs to $\mathfrak{H}'_{\mathfrak{H}}$ [8], p. 227; 10), p. 213]. Then we can show

Lemma 5.4. $\mathfrak{H}''_{\mathfrak{H}}$ is a complete vector lattice by letting $F_1 \searrow F_2$ mean that $F_1(\lambda) \searrow F_2(\lambda)$ almost everywhere.

Proof. Let $\mathfrak{H}''_{\mathfrak{H}} = \mathbf{R}(H)$ and $E(\lambda)$ be the resolution of the identity corresponding to H , and let $\mathfrak{M}$ and $\mathfrak{N}$ be two closed linear manifolds defined in [8], p. 189]. Let ψ_i , $i=1, 2, \dots$, and φ_k , $k=1, 2, \dots$, be elements of $\mathfrak{H}$ defined in [8], pp. 247, 250]. Then we consider an element ψ_0 of $\mathfrak{H}$ such that

$$\psi_0 = \alpha_1 \psi_1 + \sum_k \beta_k \varphi_k, \quad \alpha_1 \neq 0, \quad \beta_k \geq 0, \quad k=1, 2, \dots$$

Any element $\psi \in \mathfrak{H}$ can be expanded as follows,

$$\psi = \sum_i \gamma_i \psi'_i + \sum_k \delta_k \varphi'_k, \quad \psi'_i \in \mathfrak{M}(\psi_i), \quad \varphi'_k \in \mathfrak{N}(\varphi_k),$$

and, as $E(\lambda) \psi'_i$, $E(\lambda) \varphi'_k$ are mutually orthogonal,

$$\|E(\lambda) \psi\|^2 = \sum_i |\gamma_i|^2 \|E(\lambda) \psi'_i\|^2 + \sum_k |\delta_k|^2 \|E(\lambda) \varphi'_k\|^2.$$

From [8], p. 250], it is easy to show that there are functions $F_1(\lambda)$ and $F_2(\lambda)$ such that

$$\sum_i |\gamma_i|^2 \|E(\lambda) \psi'_i\|^2 = \int_{-\infty}^{\lambda} F_1(\lambda) d\|E(\lambda) (\alpha_1 \psi_1)\|^2,$$

$$\sum_k |\delta_k|^2 \|E(\lambda) \varphi'_k\|^2 = \int_{-\infty}^{\lambda} F_2(\lambda) d\|E(\lambda) (\sum_k \beta_k \varphi_k)\|^2,$$

with the conditions that $F_1(\lambda) = 0$ in the point spectrum of H , whereas $F_2(\lambda) \neq 0$ only in the point spectrum. Then

† The $\mathcal{O}$ -messbarkeit in 10) can be replaced by the H -measurability in 8), and furthermore, as $e \in \mathfrak{m}$, the condition that $F(0) = 0$ in 10) is not necessary.

$$\|E(\lambda)\psi\|^2 = \int_{-\infty}^{\lambda} (F_1(\lambda) + F_2(\lambda)) d\|E(\lambda)\psi_0\|^2,$$

namely $\rho(\lambda) = \|E(\lambda)\psi\|^2 \leq \rho_0(\lambda) = \|E(\lambda)\psi_0\|^2$, [8], p. 214]. Therefore H -measurable is equivalent to ρ_0 -measurable, and, as H is bounded, it will suffice to consider a finite interval $[\alpha, \beta]$ instead of $\mathfrak{R}$. It is well-known that the set of all bounded and ρ_0 -measurable functions $F(\alpha)$ modulo null functions is a complete vector lattice [6], p. 241][†], namely, $\bar{\pi}''_{\mathfrak{S}}$ is a complete vector lattice. Q.E.D.

From Lemma 5.3, we can easily show that the algebra $\pi''_{\mathfrak{S}}$ is isomorphic to the algebra m'' . Now, we can extend this as follows.

Lemma 5.5. $\pi''_{\mathfrak{S}}$ is isomorphic to m'' as an ordered vector space.

Proof. It has been shown in Lemma 5.2 that $a \geq 0$ (or $a > 0$) implies $\bar{a}_{\mathfrak{S}} \geq 0$ (or $\bar{a}_{\mathfrak{S}} > 0$). Let $\bar{a}_{\mathfrak{S}} \geq 0$ and $a \not\geq 0$. From Assumption 6, it is easy to show that there is an element $b \in m''$ such that $b > 0$ and $ab < 0$. Thus $\bar{b}_{\mathfrak{S}} > 0$ and $\bar{a}_{\mathfrak{S}}\bar{b}_{\mathfrak{S}} < 0$. It is obvious that $\bar{\pi}''_{\mathfrak{S}}$ is a lattice ordered ring, therefore $\bar{a}_{\mathfrak{S}} \geq 0$ and $\bar{b}_{\mathfrak{S}} \geq 0$ imply $\bar{a}_{\mathfrak{S}}\bar{b}_{\mathfrak{S}} \geq 0$. This is a contradiction, and so $\bar{a}_{\mathfrak{S}} \geq 0$ implies $a \geq 0$. Namely, $\pi''_{\mathfrak{S}}$ is isomorphic to m'' as an ordered vector space. Q.E.D.

From this it is easy to show that $m' = m''$, and also what follows.

Theorem 7. Let the completion by cuts of m'' be $\bar{m}''$, then $\bar{m}''$ can be identified with the set of all bounded elements of $\bar{\pi}''_{\mathfrak{S}}$, and it is isomorphic to $\bar{\pi}''_{\mathfrak{S}}$.

Proof. It is obvious that the completion by cuts of $\pi''_{\mathfrak{S}}$ is contained in $\bar{\pi}''_{\mathfrak{S}}$. As $\bar{\pi}''_{\mathfrak{S}}$ can be constructed from $\pi''_{\mathfrak{S}}$ by adding all the limits of strongly convergent sequences in $\pi''_{\mathfrak{S}}$ [9], p. 398], we can show that, for any element $F(H) \in \bar{\pi}''_{\mathfrak{S}}$, there is a sequence $\{F_n(H)\}$, $n=1, 2, \dots$, of elements of $\pi''_{\mathfrak{S}}$ such that $F_n(\lambda)$ are uniformly bounded and $F_n(\lambda) \rightarrow F(\lambda)$ almost everywhere [10], p. 210]. Then we can define a function $F_0(\lambda)$ by $F_0(\lambda) = \bigwedge_{n \in \mathbb{N}} \bigvee_{m \geq n} F_m(\lambda)$. For any $\varepsilon > 0$, there is a measurable set $M_\varepsilon \subset [\alpha, \beta]$ such that the ρ_0 -measure of $[\alpha, \beta] - M_\varepsilon$ is smaller than ε , and $\{F_n(\lambda)\}$ converges to $F(\lambda)$ uniformly on M_ε [11], p. 88, Egoroff's theorem]. Thus, for any $\delta > 0$ there is a number N such that, if $m \geq N$, $|F_m(\lambda) - F(\lambda)| < \delta$ on M_ε , and then $|F_0(\lambda) - F(\lambda)| \leq \delta$ on M_ε . As we can choose ε and δ arbitrarily, $F_0(\lambda) = F(\lambda)$ almost everywhere, namely $F(\lambda) = \bigwedge_{n \in \mathbb{N}} \bigvee_{m \geq n} F_m(\lambda)$. This means that the completion by cuts of $\pi''_{\mathfrak{S}}$ is $\bar{\pi}''_{\mathfrak{S}}$. Therefore, if we identify the corresponding elements of $\bar{m}$ and $\bar{\pi}''_{\mathfrak{S}}$, we get

$$\bar{m} \supset \bar{m}'' = \bar{\pi}''_{\mathfrak{S}} \supset m'' = \pi''_{\mathfrak{S}}.$$

As any element of $\bar{\pi}''_{\mathfrak{S}}$ is bounded, so is the corresponding element of $\bar{m}''$. Thus, the set of all bounded elements of $\bar{m}$ is $\bar{m}''$. Q.E.D.

This Theorem 7 and Lemma 3.4 show that any state $\bar{f} \in \bar{\mathfrak{S}}_m$ can be considered as a linear functional on $\bar{\pi}''_{\mathfrak{S}}$, and we get

Lemma 5.6. Considering any $\bar{f} \in \bar{\mathfrak{S}}_m$ to be a linear functional on $\bar{\pi}''_{\mathfrak{S}}$, we can show that there is an element $\psi_f \in \mathfrak{S}$ such that $\bar{f}(F(H)) = (\psi_f, F(H)\psi_f)$, for all $F(H) \in \pi''_{\mathfrak{S}}$.

[†] In 6), the theorem is slightly different but the modification is easy.

Proof. Let the characteristic function be $F_M(\lambda)$ for any μ_0 -measurable subset M of $[\alpha, \beta]$, then it is clear that $F_M(H) \in \mathfrak{M}''$. Put $f(M) = f(F_M(H))$, then $f(M)$ is a non-negative set function. From Assumptions 5 and 6, $\bar{f}$ is countably additive, and so f is a measure on $[\alpha, \beta]$ [11], p. 30]. Let $\rho_f(\lambda)$ be the corresponding function, then it is easy to show that, for any $F(H) \in \mathfrak{M}''$ [11], pp. 85, 112],

$$\bar{f}(F(H)) = \int_{-\infty}^{+\infty} \bar{F}(\lambda) d\rho_f(\lambda).$$

On the other hand, as $\bar{f}$ is absolutely continuous with respect to μ_0 -measure, there is a measurable function $F_f^2(\lambda) \geq 0$ such that [8], p. 215; 11], p. 124]

$$\rho_f(\lambda) = \int_{-\infty}^{\lambda} F_f^2(\lambda) d\rho_0(\lambda).$$

Thus

$$\bar{f}(F(H)) = \int_{-\infty}^{+\infty} \bar{F}(\lambda) F_f^2(\lambda) d(E(\lambda)\psi_0, \psi_0),$$

and similarly

$$\bar{f}(F^2(H)) = \int_{-\infty}^{+\infty} \bar{F}^2(\lambda) F_f^2(\lambda) d(E(\lambda)\psi_0, \psi_0).$$

As $\int_{-\infty}^{+\infty} \bar{F}_f^2(\lambda) d\rho_0(\lambda) = \rho_f(+\infty) = 1$, we can define $F_f(H)\psi_f = \psi_f \in \mathfrak{H}^{\mathfrak{M}}_f$ [8], p. 226], and

$$\bar{f}(F(H)) = \int_{-\infty}^{+\infty} \bar{F}(\lambda) d(E(\lambda)\psi_f, \psi_f),$$

$$\bar{f}(F^2(H)) = \int_{-\infty}^{+\infty} \bar{F}^2(\lambda) d(E(\lambda)\psi_f, \psi_f).$$

These imply that ψ_f is in the domain of $F(H)$ and $\bar{f}(F(H)) = (\psi_f, F(H)\psi_f)$. Q.E.D.

Theorem 8. $\mathfrak{M}$ can be represented by a vector lattice of H -measurable functions, and for any $\bar{f} \in \mathfrak{S}_{\mathfrak{M}}$

$$\bar{f}(a) = (\psi_f, F_a(H)\psi_f),$$

where $F_a(\lambda)$ is the corresponding function of $a \in \mathfrak{M}$. $F_a(H)$ is self-adjoint, and if $F_a(\lambda)$ is bounded, so is a .

Proof. Let $a \in \mathfrak{M}$, $a > 0$, and $a_n = a \cap ne$, $n=1, 2, \dots$, then $a_n \uparrow a$, $a_n \in \mathfrak{M}''$. Let the corresponding functions of a_n be $F_n(\lambda)$, then there is an extended real valued function $F_a(\lambda)$ such that $\lim_{n \rightarrow +\infty} F_n(\lambda) = F_a(\lambda)$ almost everywhere [11], p. 2]. As $F_n(\lambda)$ is H -measurable, $F_a(\lambda)$ is also H -measurable [8], p. 227; 11], p. 84]. Let f , $\rho_f(\lambda)$, and ψ_f be as in Lemma 5.6, then, for any $\rho_f(\lambda)$ [11], p. 112],

$$\lim_{n \rightarrow +\infty} \int_{-\infty}^{+\infty} F_n(\lambda) d\rho_f(\lambda) = \int_{-\infty}^{+\infty} F_a(\lambda) d\rho_f(\lambda).$$

As $\bar{f}(a_n) = \int_{-\infty}^{+\infty} F_n(\lambda) d\rho_f(\lambda)$ and $\bar{f}(a_n) \rightarrow \bar{f}(a)$, $F_a(\lambda)$ is integrable and

$$\bar{f}(a) = \int_{-\infty}^{+\infty} F_a(\lambda) d\rho_f(\lambda) = \int_{-\infty}^{+\infty} F_a(\lambda) d\|E(\lambda)\psi_f\|^2.$$

In the same way we can show that $\bar{f}(a^2) = \int_{-\infty}^{+\infty} F_a^2(\lambda) d\|E(\lambda)\phi_f\|^2$ exists, and so ϕ_f is in the domain of $F_a(H)$ [8], p. 222]. Thus

$$\bar{f}(a) = \int_{-\infty}^{+\infty} F_a(\lambda) d\rho_f(\lambda) = (\phi_f, F_a(H)\phi_f).$$

If $a \not\geq 0$, put $a = a^+ - a^-$, and $F_a(\lambda) = F_{a^+}(\lambda) - F_{a^-}(\lambda)$. As $F_a(\lambda)$ is real, $F_a(H)$ is self-adjoint [8], p. 232], and $\bar{f}(a) = (\phi_f, F_a(H)\phi_f)$. The remainder of the theorem is obvious. Q.E.D.

§ 6. Concluding remarks

On the Assumptions (1~8), we have shown that the set of field quantities can be represented by an algebra of operators in a separable Hilbert space. It goes without saying that there may be a case in which some of our assumptions are not fulfilled. We can assume, for instance, that for any two field quantities the product is not necessarily defined. Even in such a case, however, it will be natural to assume that some subsets of field quantities satisfy the assumptions in this paper, and adding some other appropriate assumptions, we shall be able to show that the set of field quantities can be represented by a subset of operators in a separable Hilbert space. Anyhow, it will not be necessary to consider a case in which field quantities are essentially different from the operators in a separable Hilbert space.

On the other hand, we have shown in § 5 that, on any $\mathfrak{M}$, $\bar{f} \in \mathfrak{S}_{\mathfrak{M}}$ can be represented by $\bar{f}(a) = (\phi_f, a_{\mathfrak{S}}\phi_f)$, $\phi_f \in \mathfrak{S}$. But, on $\mathfrak{U}$, we do not know whether any state f can be represented in like manner or not[†]. We may say in a rough sense that, in quantum mechanics, a pure state can be determined by its behavior on $\mathfrak{M}$, and that any state can be represented by these pure states. From the physical point of view, therefore, it will be quite natural to assume that $f(a) = (\phi_f, a_{\mathfrak{S}}\phi_f)$ for any $a \in \mathfrak{U}$.

Throughout the present paper we have not touched upon the physical meaning of states and field quantities themselves. For example, a *state* may be a state at one time as in the Schrödinger representation or a state independent of time as in the Heisenberg representation or a state of some other meaning. We only assert that, when states and field quantities satisfy the Assumptions (1~8), these field quantities can be represented by operators in a separable Hilbert space. Therefore, we may construct many different physical theories in this framework. In the next paper we shall mainly consider this problem and study the characteristics of field theories.

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[†] As any element of $\mathfrak{U}$ is not necessarily bounded, there may be a case where $\phi_f \in \mathfrak{S}$ is not in the domain of $a_{\mathfrak{S}}$.

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Theory of Line-Shapes of the Exciton Absorption Bands

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A general theory of line-shapes of the exciton absorption bands is developed with the help of generating function method. When the exciton-lattice coupling is weak, and the exciton effective mass is small, the absorption band is of a Lorentzian shape, provided that the temperature T is not too high. The half-value width H is given by the level broadening of the optically produced $\mathbf{K}=0$ exciton due to lattice scattering, so that it is proportional to T except at low temperatures. If the coupling is strong, or the exciton effective mass is large, or the temperature is very high, the absorption band is expected to be of a Gaussian shape, and H is proportional to $\sqrt{T}$. The mutual influence of adjacent absorption bands is also discussed; it causes the asymmetry and repulsion of the components as temperature rises.

If we replace T by the density of lattice imperfections, the above statements are valid, without substantial modifications, as regards the dependence on the degree of imperfections.

These conclusions are in qualitative agreement with experimental data. The comparison further provides us with information on the strength of the exciton-lattice coupling and the energy band structure of the exciton.

§ 1. Introduction

Since the "exciton" model was first introduced by Frenkel,¹⁾ and was applied to the explanation of several sharp peaks which are observed on the low energy sides of characteristic absorption bands in typical insulating crystals, most of theoretical attention was directed to the electronic structure of the exciton.²⁾⁻⁸⁾ Results of calculations can be compared with the experimental data, as regards peak positions,²⁾⁻⁵⁾ oscillator strengths,⁶⁾ multiplet structures^{7), 8)} and so on. However, the observed peak position corresponds to the energy of the exciton with wave number $\mathbf{K}$ nearly equal to zero, so that it does not directly give us the information on the energy band structure of the exciton.

On the other hand, the problem of exciton-phonon interaction has been attacked by several authors; some dealt with the stationary state problem of the exciton phonon system,^{9), 10)} while others calculated the probability for the scattering of an exciton by phonons.¹¹⁾ To relate these results directly with experimental data seems rather difficult, at least in the present stage.

As for the line-shapes of the exciton absorption bands, however, it does not seem that remarkable progress has been made on the theoretical side since the pioneer work by Peierls.¹²⁾ It is the purpose of the present paper to develop a general theory of the line-shape in such a way that as much information as possible is obtained through comparison with experiments. We also wish that it could contribute to inter-relating more closely the theoretical and experimental works stated above.

In § 2 of this paper, the exciton-lattice interaction Hamiltonian H_{el} is derived with Wannier's exciton wave function, including the effective mass approximation as a special case. A general formula for the optical absorption coefficient of this electron (exciton)-lattice system is derived, in § 3, as a function of the radiation frequency. The Fourier transform of the absorption coefficient, that is, the generating function, is expanded into an infinite power series H_{el} . In the two extreme cases, that is, weak and strong limits of the coupling H_{el} , the series can be brought into simpler expressions. Thus, in the limit of weak coupling (§ 4), the absorption band tends to a Lorentzian shape due to the motional effect of the exciton. In the opposite limit the band takes a Gaussian shape, which means that the "localized exciton" model is valid in this case (§ 5). In the intermediate region, the absorption band may show an asymmetry, depending upon the energy band structure of the exciton.

When two or more exciton absorption bands lie very close to each other, the influence of each component on the strengths, peak positions and shape asymmetries of other components becomes important, as is discussed in § 6.

§ 7 is devoted to the derivation of criterion for the appearance of two extreme cases in a more explicit form, and to the arrangement of theoretical conclusions so as to be convenient for comparison with experimental data. In § 8 we carried out the analysis of a few of experimental data available, which proves to be in satisfactory agreement with theoretical expectations.

Further information is obtained through this comparison: one is the strength of the exciton-lattice coupling, and the other concerns the energy band structure of the exciton. They will be utilized, in the next paper, for speculative investigations of the various dynamical processes which the exciton possibly suffers.¹³⁾

§ 2. The derivation of exciton-lattice interaction Hamiltonian

Let us consider an insulating crystal consisting of N atoms and N valence electrons, and denote the Wannier functions¹⁾ for valence and conduction bands by $a_v(\mathbf{x}, m)$ and $a_c(\mathbf{x}, n)$, respectively, where m and n refer to lattice sites.

In the approximation of one electron excitation, the wave function for an exciton with inner quantum number λ and translational wave-number $\mathbf{K}$ is given by¹⁾

$$\Psi_{\lambda\mathbf{K}} = N^{-1/2} \sum_m \exp(i\mathbf{K} \cdot \mathbf{m}) \sum_l U_{\lambda\mathbf{K}}(\mathbf{l}) A(\mathbf{m}, \mathbf{m} + \mathbf{l}), \quad (2 \cdot 1)$$

where $A(\mathbf{m}, \mathbf{n})$ is the Slater determinant of N electrons for the configuration $\{a_v(\mathbf{x}, 1), a_v(\mathbf{x}, 2), \dots, a_v(\mathbf{x}, m-1), a_c(\mathbf{x}, n), a_v(\mathbf{x}, m+1), \dots, a_v(\mathbf{x}, N)\}$, that is, the configuration in which the valence electron of the m -th site is excited into the conduction band, at the n -th site. The wave function $U_{\lambda\mathbf{K}}(\mathbf{l})$ for the relative motion of the electron and the hole is to be determined from Wannier's difference equation, with Hamiltonian $H_{el} = T + V$, where T is the sum of the energies of the electron and the hole, and V denotes Coulomb and exchange interactions between them.

If we make use of the effective mass approximation, the kinetic term T , as an operator on $U_{\lambda\mathbf{K}}(\mathbf{l})$, can be replaced by a differential operator $\mathcal{W}(-i \cdot \partial / \partial \mathbf{l}, \mathbf{K})$, where

$$W(\mathbf{k}, \mathbf{K}) \equiv -W_v(\mathbf{k}-\mathbf{K}) + W_c(\mathbf{k}), \quad (2.2)$$

and $W_v(\mathbf{k})$, $W_c(\mathbf{k})$ mean the one electron energies, with wave number $\mathbf{k}$, of the valence and conduction bands, respectively. For a fixed value of $\mathbf{K}$, one can expand $W(\mathbf{k}, \mathbf{K})$ around a minimum point $\mathbf{k}_m(\mathbf{K})$:

$$W(\mathbf{k}, \mathbf{K}) = J(\mathbf{K}) + (\mathbf{k} - \mathbf{k}_m(\mathbf{K})) \cdot \hbar^2 / 2\mu(\mathbf{K}) \cdot (\mathbf{k} - \mathbf{k}_m(\mathbf{K})) + \dots, \quad (2.3)$$

the coefficient $\mu(\mathbf{K})$ being a reduced mass tensor. If we transform the wave function by

$$\varphi_{\lambda\mathbf{K}}(\mathbf{l}) = e^{-i\mathbf{k}_m(\mathbf{K})\mathbf{l}} U_{\lambda\mathbf{K}}(\mathbf{l}), \quad (2.4)$$

T is replaced by

$$J(\mathbf{K}) - \partial/\partial\mathbf{l} \cdot \hbar^2 / 2\mu(\mathbf{K}) \cdot \partial/\partial\mathbf{l}. \quad (2.5)$$

The potential part V , in this new representation, is written as

$$\begin{aligned} (l|V|l') &= -e^{i\mathbf{k}_m(\mathbf{K})(\mathbf{l}-\mathbf{l}')} \sum_{\mathbf{p}} e^{i\mathbf{K}\mathbf{p}} \iint a_v(\mathbf{x}, 0) a_v^*(\mathbf{x}, \mathbf{p}) \\ &\quad \times e^2/|\mathbf{x}-\mathbf{x}'| \cdot a_c^*(\mathbf{x}', \mathbf{l}) a_c(\mathbf{x}', \mathbf{p}+\mathbf{l}') d\mathbf{x} d\mathbf{x}' \\ &\quad + e^{i\mathbf{k}_m(\mathbf{K})(\mathbf{l}-\mathbf{l}')} \sum_{\mathbf{p}} e^{i\mathbf{K}\mathbf{p}} \iint a_v(\mathbf{x}, 0) a_v^*(\mathbf{x}', \mathbf{p}) \\ &\quad \times e^2/|\mathbf{x}-\mathbf{x}'| \cdot a_c^*(\mathbf{x}, \mathbf{l}) a_c(\mathbf{x}', \mathbf{p}+\mathbf{l}') d\mathbf{x} d\mathbf{x}'. \end{aligned} \quad (2.6)$$

It reduces to a Coulomb attraction $-\delta_{ll'} e^2/|l|$ in the crudest approximation, as is well known.

If we make further simplification by taking parabolic approximation for both of the energy bands:

$$\begin{aligned} W_v(\mathbf{k}) &= -(\mathbf{k}-\mathbf{k}_v) \cdot \hbar^2 / 2m_h \cdot (\mathbf{k}-\mathbf{k}_v), \\ W_c(\mathbf{k}) &= \varepsilon_g + (\mathbf{k}-\mathbf{k}_c) \cdot \hbar^2 / 2m_e \cdot (\mathbf{k}-\mathbf{k}_c), \end{aligned} \quad (2.7)$$

we have

$$\begin{aligned} \mathbf{k}_m(\mathbf{K}) &= p_h \cdot (\mathbf{k}_v + \mathbf{K}) + p_e \cdot \mathbf{k}_c, \\ J(\mathbf{K}) &= \varepsilon_g + \mathbf{K}^* \cdot \hbar^2 / 2m^* \cdot \mathbf{K}^*, \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} m^* &\equiv m_e + m_h, \quad \mu^{-1} \equiv m_h^{-1} + m_e^{-1}, \\ p_h &\equiv \mu \cdot m_h^{-1} = m_e \cdot m^{*-1}, \quad p_e \equiv \mu \cdot m_e^{-1} = m_h \cdot m^{*-1}, \\ \mathbf{K}^* &\equiv \mathbf{K} - \mathbf{K}_0, \quad \mathbf{K}_0 \equiv \mathbf{k}_c - \mathbf{k}_v. \end{aligned} \quad (2.9)$$

The result is shown in Fig. 1 schematically. Because of symmetry, of course, there are actually equivalent branches on the opposite sides.

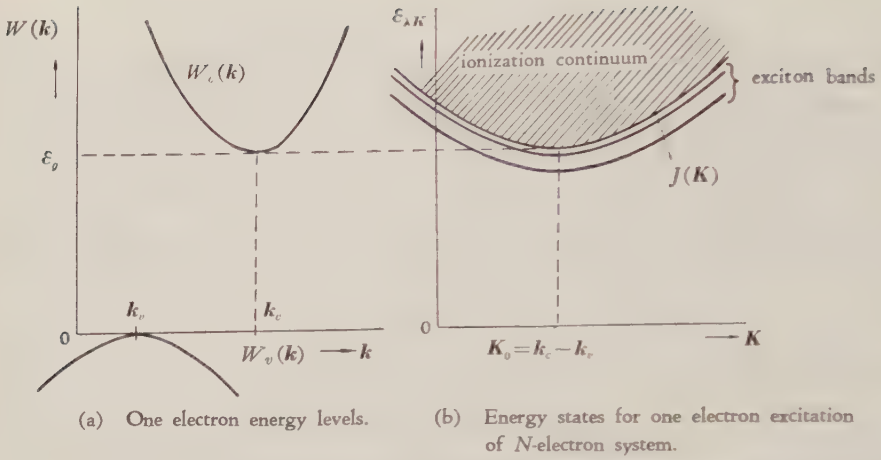


Fig. 1. Energy level scheme in the effective mass approximation.

We now consider the change of the potential energy between electrons and lattice, caused by an arbitrary lattice deformation: it is the sum of N equivalent one-electron energies:

$$\delta H_e(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_{i=1}^N \delta H_1(\mathbf{x}_i). \quad (2 \cdot 10)$$

Making use of the relation

$$\begin{aligned} (A(\mathbf{m}, \mathbf{n}) | \delta H_e | A(\mathbf{m}', \mathbf{n}')) &= -\delta_{nn'} \int a_v(\mathbf{x}, \mathbf{m}) \delta H_1 \times a_v^*(\mathbf{x}, \mathbf{m}') d\mathbf{x} \\ &\quad + \delta_{mm'} \int a_c^*(\mathbf{x}, \mathbf{n}) \delta H_1 a_c(\mathbf{x}, \mathbf{n}') d\mathbf{x}, \end{aligned}$$

and then transforming the Wannier functions into the Bloch orbitals $b_v(\mathbf{x}, \mathbf{k})$ and $b_c(\mathbf{x}, \mathbf{k})$, we have

$$\begin{aligned} (\Psi_{\lambda K} | \delta H_e | \Psi_{\lambda' K'}) &= -N^{-1} \sum_l \sum_{l'} \sum_k U_{\lambda K}^*(l) U_{\lambda' K'}(l') \exp \{i(\mathbf{K} + \mathbf{k})(l - l')\} \\ &\quad \times \Xi_v(\mathbf{k} + \mathbf{K} - \mathbf{K}', \mathbf{k}) + N^{-1} \sum_l \sum_{l'} \sum_k U_{\lambda K}^*(l) U_{\lambda' K'}(l') \\ &\quad \times \exp \{i(\mathbf{K} - \mathbf{K}')l + i\mathbf{k}(l - l')\} \Xi_c(\mathbf{k}, \mathbf{k} - \mathbf{K} + \mathbf{K}'), \end{aligned} \quad (2 \cdot 11)$$

where

$$\Xi_v(\mathbf{k}, \mathbf{k}') \equiv \int b_v^*(\mathbf{x}, \mathbf{k}) \delta H_1(\mathbf{x}) b_v(\mathbf{x}, \mathbf{k}') d\mathbf{x} \quad (2 \cdot 12)$$

is the usual scattering matrix element of an electron-lattice system.

The lattice distortion, which causes $\delta H_1(\mathbf{x})$, may be an instantaneous position of thermal vibration, or a static deformation due to any kind of lattice imperfections such

as dislocations. For the acoustic mode of vibration we can take (i) the *deformable atom approximation* due to Bloch and Bethe¹¹⁾ or (ii) the *deformation potential* introduced by Bardeen and Shockley,¹³⁾ as the case may be. In the case of optical mode of vibration in ionic crystals, δH_1 is nothing but the electrostatic field due to the polarization of the lattice, and was given by (iii) Fröhlich *et al.*¹⁶⁾ Throughout these three cases (2.12) depends only on $(\mathbf{k}-\mathbf{k}')$, that is, $\Xi_v(\mathbf{k}, \mathbf{k}') \equiv \hat{\xi}_v(\mathbf{k}-\mathbf{k}')$, and (2.11) is written as

$$-q_h(\lambda\mathbf{K}, \lambda'\mathbf{K}')\hat{\xi}_v(\mathbf{K}-\mathbf{K}') + q_e(\lambda\mathbf{K}, \lambda'\mathbf{K}')\hat{\xi}_c(\mathbf{K}-\mathbf{K}'). \quad (2.13)$$

If one takes the effective mass approximation (2.2) $\sim$ (2.9), which is tacitly assumed also when one calculates (2.12) in the three cases (i) $\sim$ (iii) stated above, q can be expressed as

$$\left. \begin{aligned} q_h(\lambda\mathbf{K}, \lambda'\mathbf{K}') &\equiv \sum_{\mathbf{l}} U_{\lambda\mathbf{K}}^*(\mathbf{l}) U_{\lambda'\mathbf{K}'}(\mathbf{l}) \\ &= \sum_{\mathbf{l}} \varphi_{\lambda}^*(\mathbf{l}) \varphi_{\lambda'}(\mathbf{l}) \exp\{-i(\mathbf{K}-\mathbf{K}') \cdot \mathbf{p}_h \cdot \mathbf{l}\} \equiv q_h(\mathbf{K}-\mathbf{K}'; \lambda\lambda'), \\ q_e(\lambda\mathbf{K}, \lambda'\mathbf{K}') &\equiv \sum_{\mathbf{l}} U_{\lambda\mathbf{K}}^*(\mathbf{l}) U_{\lambda'\mathbf{K}'}(\mathbf{l}) \exp\{i(\mathbf{K}-\mathbf{K}') \cdot \mathbf{l}\} \\ &= \sum_{\mathbf{l}} \varphi_{\lambda}^*(\mathbf{l}) \varphi_{\lambda'}(\mathbf{l}) \exp\{+i(\mathbf{K}-\mathbf{K}') \cdot \mathbf{p}_e \cdot \mathbf{l}\} \equiv q_e(\mathbf{K}-\mathbf{K}'; \lambda\lambda'). \end{aligned} \right\} \quad (2.14)$$

We now introduce, for convenience, the creation-annihilation operators $a_{\lambda\mathbf{K}}^*$, $a_{\lambda\mathbf{K}}$ for the $(\lambda\mathbf{K})$ -exciton, whose energy we denote by $\varepsilon_{\lambda\mathbf{K}}$, and the creation-annihilation operators $b_{\mu\mathbf{w}}^*$, $b_{\mu\mathbf{w}}$ for the $(\mu\mathbf{w})$ -phonon with energy quantum $\hbar\omega_{\mu\mathbf{w}}$, where μ and $\mathbf{w}$ refer to the mode and the wave number of the phonon. a and a^* satisfy approximately the commutation relations for bosons, but this is immaterial as far as we confine ourselves to the electronic states in which the total number of excitons is zero or unity, as we do in later discussions. The Hamiltonian of the electron system and that of the lattice system are now written as

$$\left. \begin{aligned} H_e &= \sum_{\lambda\mathbf{K}} \varepsilon_{\lambda\mathbf{K}} a_{\lambda\mathbf{K}}^* a_{\lambda\mathbf{K}}, \\ H_L &= \sum_{\mu\mathbf{w}} \hbar\omega_{\mu\mathbf{w}} b_{\mu\mathbf{w}}^* b_{\mu\mathbf{w}}, \end{aligned} \right\} \quad (2.15)$$

respectively, whereas the interaction between them is written, in linear approximation but otherwise quite generally, as

$$H_{eL} = \sum_{\mu} \sum_{\lambda\mathbf{K}} \sum_{\lambda'\mathbf{K}'} i(\lambda\mathbf{K}|\beta_{\mu}|\lambda'\mathbf{K}') (b_{\mu, \mathbf{K}-\mathbf{K}'} - b_{\mu, -\mathbf{K}+\mathbf{K}'}^*) a_{\lambda\mathbf{K}}^* a_{\lambda'\mathbf{K}'}. \quad (2.16)$$

In the three cases (i) $\sim$ (iii) stated above, we have explicit expressions for the matrix element (2.12), and $(\lambda\mathbf{K}|\beta_{\mu}|\lambda'\mathbf{K}')$ depends on $\mathbf{K}$ and $\mathbf{K}'$ only through $\mathbf{K}-\mathbf{K}'$ as is seen from (2.13) and (2.14). If we write $(\lambda\mathbf{K}|\beta_{\mu}|\lambda'\mathbf{K}') = \beta_{\mu}(\mathbf{K}-\mathbf{K}'; \lambda\lambda')$, it is given by

$$\left. \begin{aligned} \beta_{ac}(\mathbf{w}; \lambda\lambda') &= (2\hbar/9NMu)^{1/2} \mathbf{w}^{1/2} \{-q_h(\mathbf{w}; \lambda\lambda') C_v + q_e(\mathbf{w}; \lambda\lambda') C_c\}, \\ \beta_{op}(\mathbf{w}; \lambda\lambda') &= \{2\pi\hbar\omega e^2/Nv_0 \cdot (1/\kappa_0 - 1/\kappa)\}^{1/2} 1/\mathbf{w} \cdot \{-q_h(\mathbf{w}; \lambda\lambda') + q_e(\mathbf{w}; \lambda\lambda')\}, \end{aligned} \right\} \quad (2.17)$$

for the acoustic and optical modes, respectively. In case (i) C is nothing but the kinetic energy of the Bloch function, whereas in case (ii) $-2C/3$ is the so-called deformation potential, that is, the energy change of the band bottom (or the top) due to unit dilation of lattice. M and v_0 denote the mass and the volume of a unit cell, κ and κ_0 are static and optical dielectric constants. u is an average sound velocity and $\omega/2\pi$ is the frequency of optical vibration, both referring to longitudinal waves. Ansel'm and Firsov¹¹⁾ used (2.17) for the calculation of the mean free path of an exciton, confining themselves to the case $\lambda \neq \lambda'$ ($=1s$ -state), that is, to the *intra* band scattering, whereas Haken¹²⁾ took into account the *interband* term $\lambda \neq \lambda'$ for the calculation of the self-energy of an exciton. Note that we can use (2.17) with (2.14), even when $\mathbf{k}_e \neq \mathbf{k}_h \neq 0$.

$q(\mathbf{w})$ in (2.14) is the Fourier transform of the charge distributions of the electron or the hole in the internal motion, because $p_e \cdot \mathbf{l}$, for instance, is the electron coordinate relative to the center of mass. It represents the effectivity of the electron or hole charge for a particular phonon $\mathbf{w}$. Now, $q(\mathbf{w}, \lambda\lambda')$ tends to unity or zero as w tends to zero, according as $\lambda = \lambda'$ or $\lambda \neq \lambda'$, while, in any case, it becomes very small when the wave length $2\pi/w$ of the phonon is smaller than the radius of the exciton, that is, the mean distance between the electron and the hole. For example, in the case of the $1s$ -state of the relative motion with decay constant α , we have

$$q_e(\mathbf{w}; 1s1s) = \{1 + (p_e w/2\alpha)^2\}^{-2}. \quad (2.18)$$

(2.17) tells us that the optical mode is probably less important than the acoustic mode for the *intra*band scattering of an exciton, for $\beta_z(\mathbf{w})$ tends to zero as w when w tends to zero, whereas $\beta_{ac}(\mathbf{w})$ tends to zero as $w^{1/2}$; further it is in contrast with $\beta_{op}(\mathbf{w}) \propto w^{-1}$ for the case of a single electron. To the *interband* scattering, however, both modes would make comparable contributions, because only the phonons with finite w would play a rôle in this case, due to the energy conservation.

§ 3. A general formula for the absorption coefficient

The Hamiltonian for the electron-lattice system is written as

$$H = H_e + H_L + H_{eL}, \quad (3.1)$$

where H_e , H_L and H_{eL} are given by (2.15) and (2.16). We now derive the coefficient of the optical absorption of this system which corresponds to the creation of an exciton.

Consider a radiation field R in the crystal medium which is assumed to be isotropic with refractive index n . Its Hamiltonian is given by

$$H_R = \sum_{\sigma, \mathbf{K}} \hbar \omega_{\mathbf{K}} c_{\sigma \mathbf{K}}^* c_{\sigma \mathbf{K}}, \quad \omega_{\mathbf{K}} = (c/n)K, \quad (3.2)$$

where $\sigma (=1, 2)$ and $\mathbf{K}$ refer to the polarization (the directions being denoted by unit vectors $\mathbf{e}_{\sigma \mathbf{K}}$) and wave-number of the photon, and $c_{\sigma \mathbf{K}}^*$ and $c_{\sigma \mathbf{K}}$ mean the creation-annihilation operators. c is the light velocity in vacuum. Strictly speaking, n is not constant in the frequency range we are considering; on the contrary, the absorption itself contributes to the dispersion of n . The most satisfactory way would be to determine n and absorption

efficient self-consistently. To avoid this rather complicated problem of dispersion relation, we take n to be constant over a range of frequency and equal to an appropriate average value.

It is sufficient, for the present purpose, to take into account the interaction of R with the electron system alone, H_{eR} , because in the frequency range at issue ($\omega \sim 10^{16}$ sec $^{-1}$), the vibration of lattice cannot follow that of the radiation field. Thus the total Hamiltonian is written as

$$H_{\text{tot}} = H + H_R + H_{eR}. \quad (3.3)$$

Denoting the number of $(\sigma\mathbf{K})$ -photons by $m_{\sigma\mathbf{K}}$, the matrix element of H_{eR} which corresponds to the absorption of a $(\sigma\mathbf{K})$ -photon with simultaneous creation of a $(\lambda\mathbf{K})$ -exciton is calculated as

$$\begin{aligned} & (\Psi_{\lambda\mathbf{K}}; \dots, m_{\sigma\mathbf{K}} - 1, \dots | H_{eR} | \Psi_0; \dots, m_{\sigma\mathbf{K}}, \dots) \\ &= ie\hbar/mc (2\pi\hbar c m_{\sigma\mathbf{K}}/v_0 nK)^{1/2} (\mathbf{e}_{\sigma\mathbf{K}} \cdot \mathbf{g}_{\lambda\mathbf{K}}), \end{aligned} \quad (3.4)$$

where

$$\begin{aligned} \mathbf{g}_{\lambda\mathbf{K}} &\equiv N^{-1/2} \int \dots \int \Psi_{\lambda\mathbf{K}}^* \sum_{i=1}^N \nabla_i e^{i\mathbf{K}\mathbf{x}_i} \Psi_0 d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \sum_l U_{\lambda\mathbf{K}}^*(\mathbf{l}) \int a_e^*(\mathbf{x}, \mathbf{l}) \nabla e^{i\mathbf{K}\mathbf{x}} a_v(\mathbf{x}, 0) d\mathbf{x}. \end{aligned} \quad (3.5)$$

Let us now assume that initially the electron system is in the ground state Ψ_0 (no exciton), the lattice system in state Φ_n and the radiation field in state X_m . At the time T , the wave function of the total system is given by

$$\begin{aligned} & e^{-iH_{\text{tot}}T/\hbar} \Psi_0 \Phi_n X_m \\ &= e^{-i(H+H_R)T/\hbar} \left[1 - i/\hbar \int_0^T e^{i(H+H_R)t_1/\hbar} H_{eR} e^{-i(H+H_R)t_1/\hbar} dt_1 + \dots \right] \Psi_0 \Phi_n X_m. \end{aligned} \quad (3.6)$$

In the lowest order of perturbation, let us take, out of (3.6), the term corresponding to the state in which a $(\sigma\mathbf{K})$ -photon is absorbed and an exciton (with any λ) is created:

$$\begin{aligned} & e/mc \cdot (2\pi\hbar c m_{\sigma\mathbf{K}}/v_0 nK)^{1/2} e^{-i(m_{\sigma\mathbf{K}}-1)\omega_{\sigma\mathbf{K}}T} \sum_{\lambda} (\mathbf{e}_{\sigma\mathbf{K}} \cdot \mathbf{g}_{\lambda\mathbf{K}}) \\ & \times \int_0^T e^{-i\omega_{\sigma\mathbf{K}}t_1} e^{-iH(T-t_1)/\hbar} \Psi_{\lambda\mathbf{K}} e^{-iH_L t_1/\hbar} \Phi_{d_1} X_{\dots, m_{\sigma\mathbf{K}}-1, \dots} \end{aligned} \quad (3.7)$$

Taking the absolute square of (3.7), and averaging over the initial distribution $n = (\dots, n_w, \dots)$ of vibrational states, we have, as the probability for that state to be realized,

$$W(m_{\sigma K}, T) = (e/mc)^2 2\pi\hbar c m_{\sigma K} / v_0 n_K \cdot \sum_{\lambda} \sum_{\lambda'} (e_{\sigma K} \cdot g_{\lambda K}^*) (e_{\sigma K} \cdot g_{\lambda' K}) \\ \times \int_0^T dt_1 \int_{-t_1}^{T-t_1} dt e^{i\omega_{\sigma K} t} \{ (\lambda K | e^{-iHt/\hbar} | \lambda' K) e^{iH_L t/\hbar} \}_{Av}. \quad (3.8)$$

Here

$$\{\dots\}_{Av} \equiv \text{Tr}_L [e^{-\beta H_L} \{\dots\}] / \text{Tr}_L (e^{-\beta H_L}), \quad (3.9)$$

Tr_L referring to the lattice system alone, and $(\kappa\beta)^{-1}$ being the absolute temperature.

When T is large enough in (3.8), most of the contributions to $\int_0^T dt_1$ come from large values of t_1 and $T-t_1$, so that we can replace the upper and lower bound of the second integration by $\pm\infty$. Dividing by $Tm_{\sigma K}$, the lifetime τ of (σK) -photon is given by

$$1/\tau(\sigma K) = (e/mc)^2 2\pi\hbar c^2 / v_0 n^2 \omega_{\sigma K} \cdot \sum_{\lambda} \sum_{\lambda'} (e_{\sigma K} \cdot g_{\lambda K}^*) (e_{\sigma K} \cdot g_{\lambda' K}) \\ \times \int_{-\infty}^{+\infty} dt e^{i\omega_{\sigma K} t} \{ (\lambda K | e^{-iHt/\hbar} | \lambda' K) e^{iH_L t/\hbar} \}_{Av}. \quad (3.10)$$

The absorption coefficient is defined as the reciprocal of penetration depth for which the radiation attenuates to e^{-1} . It is given, for the frequency $\omega = cK/n$, by

$$A(\omega) = n/c \cdot 1/2 \cdot \sum_{\sigma} 1/\tau(\sigma, K), \quad (3.11)$$

where average was taken for the two directions of polarization.

(3.10) is nothing but the method of generating function (or the method of Fourier transform) which was applied to the radiative and non-radiative transitions of a trapped electron.^{17),18)} In the present case, however, we cannot generally use the adiabatic approximation for the electron-lattice system H , because the exciton energy levels constitute continuous spectra due to the translational motion. We proceed in another way, and expand the exponential in (3.10):

$$e^{-iHt/\hbar} = e^{-i(H_e + H_L)t/\hbar} \sum_{n=0}^{\infty} (i\hbar)^{-n} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \cdot H'(t_1) \cdots H'(t_n), \quad (3.12)$$

where

$$H'(t) \equiv e^{i(H_e + H_L)t/\hbar} H_{eL} e^{-i(H_e + H_L)t/\hbar} \\ = i \sum_{\mu} \sum_{\lambda\lambda'} \sum_{Kw} \beta_{\mu\lambda\lambda'}(\mathbf{w}) e^{i(\varepsilon_{\lambda K} + \varepsilon_w - \varepsilon_{\lambda' K})t/\hbar} \\ \times a_{\lambda K + w}^* a_{\lambda' K} (b_{\mu w} e^{-i\omega_{\mu} w t} - b_{\mu, -w}^* e^{i\omega_{\mu} w t}). \quad (3.13)$$

Defining

$$F_{\lambda\lambda'}(\mathbf{K}) \equiv 1/2 \cdot \sum_{\sigma} (e_{\sigma K} \cdot g_{\lambda K}^*) (e_{\sigma K} \cdot g_{\lambda' K}), \quad (3.14)$$

we have an infinite series expression for the absorption coefficient :

$$A(\omega) = 2\pi\hbar e^2/m^2 v_0 c n \omega_{\mathbf{K}} \cdot \sum_{\lambda} \sum_{\lambda'} F_{\lambda\lambda'}(\mathbf{K}) \times \int_{-\infty}^{+\infty} dt e^{i\omega t - i\varepsilon_{\lambda}\mathbf{K}t/\hbar} \sum_n U_n(t; \lambda\lambda'; \mathbf{K}), \quad (3.15)$$

where

$$U_n(t; \lambda\lambda'; \mathbf{K}) = (i\hbar)^{-n} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n (\lambda\mathbf{K} | H'(t_1) \cdots H'(t_n) | \lambda'\mathbf{K})_{Av}. \quad (3.16)$$

As $H'(t)$ of (3.13) is linear in the lattice co-ordinates $b_{\mu w}$ and $b_{\mu w}^*$, U_n vanishes for odd n . The first two terms are given by

$$U_0(t; \lambda\lambda'; \mathbf{K}) = \delta_{\lambda\lambda'}, \quad (3.17)$$

$$U_2(t; \lambda\lambda'; \mathbf{K}) = -\hbar^{-2} \int_0^t d\tau \int_{\tau}^t dt_1 \sum_{\mu} \sum_{\lambda_1} \sum_w \beta_{\mu\lambda_1\lambda}(-\mathbf{w}) \times \beta_{\mu\lambda_1\lambda'}(\mathbf{w}) e^{i(\varepsilon_{\lambda}\mathbf{K} - \varepsilon_{\lambda'}\mathbf{K})t_1/\hbar} e^{i(\varepsilon_{\lambda'}\mathbf{K} - \varepsilon_{\lambda_1}\mathbf{K} + \mathbf{w})\tau/\hbar} \times \{ (n_{\mu w} + 1) e^{-i\omega_{\mu w}\tau} + n_{\mu w} e^{i\omega_{\mu w}\tau} \}. \quad (3.18)$$

The diagonal ($\lambda=\lambda'$) term is further reduced to

$$U_2(t; \lambda\lambda; \mathbf{K}) = -\hbar^{-2} \int_0^t (t-\tau) d\tau \sum_{\mu} \sum_{\lambda_1} \sum_w |\beta_{\mu\lambda_1\lambda}(\mathbf{w})|^2 \times e^{i(\varepsilon_{\lambda}\mathbf{K} - \varepsilon_{\lambda_1}\mathbf{K} + \mathbf{w})\tau/\hbar} \{ (n_{\mu w} + 1) e^{-i\omega_{\mu w}\tau} + n_{\mu w} e^{i\omega_{\mu w}\tau} \} \quad (3.19)$$

$$= -\hbar^{-2} \int_0^t d\tau \int_{-\infty}^{+\infty} dE (t-\tau) e^{-iE\tau/\hbar} f_{\lambda\mathbf{K}}(E), \quad (3.19')$$

where

$$f_{\lambda\mathbf{K}}(E) \equiv \sum_{\mu} \sum_{\lambda_1} \sum_w |\beta_{\mu\lambda_1\lambda}(\mathbf{w})|^2 \{ (n_{\mu w} + 1) \delta(\varepsilon_{\lambda_1}\mathbf{K} + \mathbf{w} + \hbar\omega_{\mu w} - \varepsilon_{\lambda}\mathbf{K} - E) + n_{\mu w} \delta(\varepsilon_{\lambda_1}\mathbf{K} + \mathbf{w} - \hbar\omega_{\mu w} - \varepsilon_{\lambda}\mathbf{K} - E) \}. \quad (3.20)$$

§ 4. The weak coupling limit

Consider a continuous function $f(E)$, the value of which is assumed not to vary appreciably over the range ΔE , or more specifically, $|f'(E) \Delta E| \lesssim f(E)$, that is :

$$\hbar/\Delta E \gtrsim \tau_c(E) \equiv \hbar f'(E)/f(E). \quad (4.1)$$

For a value of $|t|$ much larger than τ_c , we have an asymptotic formula¹⁹⁾

$$\hbar^{-1} \int_0^t d\tau \int e^{-iE\tau/\hbar} f(E) dE \sim \int \{ \pm \pi \delta(E) - i \mathcal{P}(1/E) \} f(E) dE \quad (|t| \gtrsim \tau_c), \quad (4.2)$$

where $\pm$ correspond to $t \leq 0$. Thus (3.19') becomes

$$U_2(t; \lambda\lambda; \mathbf{K}) = -\hbar^{-2} \int_0^t d\tau \int_{-\infty}^{+\infty} dE e^{-iE\tau/\hbar} (t + i\hbar \partial/\partial E) \cdot f_{\lambda\mathbf{K}}(E) \\ = -\mathcal{P} \int f'_{\lambda\mathbf{K}}(E)/E \cdot dE \mp i\pi f'_{\lambda\mathbf{K}}(0) - (\Gamma_{\lambda\mathbf{K}}/2) |t| - itJ_{\lambda\mathbf{K}}/\hbar, \quad (4.3)$$

where

$$\Gamma_{\lambda\mathbf{K}} \equiv (2\pi/\hbar) f_{\lambda\mathbf{K}}(0) = (2\pi/\hbar) \sum_{\mu} \sum_{\lambda_1} \sum_{\mathbf{w}} |\beta_{\mu\lambda_1\lambda}(\mathbf{w})|^2 \\ \times \{ (n_{\mu\mathbf{w}} + 1) \delta(\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} - \hbar\omega_{\mu\mathbf{w}}) \\ + n_{\mu\mathbf{w}} \delta(\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} + \hbar\omega_{\mu\mathbf{w}}) \}, \quad (4.4)$$

$$J_{\lambda\mathbf{K}} \equiv -\mathcal{P} \int f(E)/E \cdot dE = \sum_{\mu} \sum_{\lambda_1} \sum_{\mathbf{w}} |\beta_{\mu\lambda_1\lambda}(\mathbf{w})| \\ \times \left\{ (n_{\mu\mathbf{w}} + 1) \frac{\mathcal{P}}{\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} - \hbar\omega_{\mu\mathbf{w}}} + n_{\mu\mathbf{w}} \frac{\mathcal{P}}{\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} + \hbar\omega_{\mu\mathbf{w}}} \right\} \quad (4.5)$$

are the probability (per unit time) of the scattering, and the self-energy, of the $(\lambda\mathbf{K})$ -exciton due to lattice vibration. $\delta(E)$ is Dirac's delta function and $\mathcal{P}$ means the principal value. Owing to $|t| \gg \tau_c$, the first two terms of (4.3) are small compared with the remaining terms; we therefore neglect the former for the present.

For the ultraviolet and visible regions of radiation, the photon wave number $\mathbf{K}$ is much smaller ($\sim 10^6 \text{ cm}^{-1}$) than the reciprocal lattice vector ($\sim 10^8 \text{ cm}^{-1}$), so that we can put $\mathbf{K} = 0$ in the above.

If we take into account only the diagonal term $\lambda = \lambda'$ in (3.15), and approximate as

$$U_0(t; \lambda\lambda; 0) + U_2(t; \lambda\lambda; 0) + \dots \\ = 1 + \{ -(\Gamma_{\lambda 0}/2) |t| - itJ_{\lambda 0}/\hbar \} + \dots \approx \exp \{ -(\Gamma_{\lambda 0}/2) |t| - itJ_{\lambda 0}/\hbar \}, \quad (4.6)$$

we have, for the contribution of λ -exciton band to the absorption coefficient (3.15),

$$A_{\lambda}(\omega) = \frac{4\pi}{3} \frac{\hbar^2 e^2 |\mathbf{g}_{\lambda 0}|^2}{m^2 v_0 c n \omega} \frac{(\hbar \Gamma_{\lambda 0}/2)}{\{ \hbar\omega - (\varepsilon_{\lambda 0} + J_{\lambda 0}) \}^2 + (\hbar \Gamma_{\lambda 0}/2)^2}. \quad (4.7)$$

(4.7) shows that the absorption band is of a Lorentzian shape, with a peak at $\varepsilon_{\lambda 0} + J_{\lambda 0}$ and a half-value width $H = \hbar \Gamma_{\lambda 0}$ (if $\Gamma_{\lambda 0} \ll \omega$ as is always the case). The latter is nothing but the broadening of $(\lambda 0)$ -level due to lattice scattering. Each absorption peak λ is expected to be free from the influence of other peaks if $|\varepsilon_{\lambda 0} - \varepsilon_{\lambda' 0}| \gg \hbar \Gamma_{\lambda 0}$ and if the contribution of interband terms $U_i(t; \lambda\lambda'; 0)$ is negligible. The latter effect will be shown, in § 6, to be small if $\partial\hbar \gg \Gamma_{\lambda} J_{\lambda}$.

Of course, our approximation fails if, for values of $|t|$ satisfying $|t| \lesssim \tau_c$, the exponential of (4.6) already decays to values much smaller than unity. Thus our approximation is valid only when $\Gamma_{\lambda 0}$ is so small that the condition

$$\Gamma_{\lambda 0} \tau_c / 2 \ll 1 \quad (4.8)$$

is satisfied, in other words, when the exciton-lattice interaction is sufficiently weak. The more explicit form of the condition will be given in § 7. In any case, at the weak coupling limit, each of $U_{2m}(t; \lambda\lambda; 0)$ ($m=0, 1, 2, \dots$) reduces to simpler form, leading to*

$$\begin{aligned} \sum_{m=0}^{\infty} U_{2m}(t; \lambda\lambda; 0) &= \sum_{m=0}^{\infty} \{-(\Gamma_{\lambda 0}/2) |t| - i t \Delta_{\lambda 0} / \hbar\}^m / m! \\ &= \exp \{-(\Gamma_{\lambda 0}/2) |t| - i t \Delta_{\lambda 0} / \hbar\}. \end{aligned} \quad (4.9)$$

Thus the approximation (4.6) proves to be exact in this limit.

Next we investigate the effect of the first two terms of (4.3). In the first approximation, we have, instead of (4.6),

$$\begin{aligned} U_0 + U_2 + \dots &\approx \{1 - \mathcal{P} \int f'(E) / E \cdot dE\} \{1 \mp i\pi f'(0)\} \\ &\times \exp \{-(\Gamma_{\lambda 0}/2) |t| - i t \Delta_{\lambda 0} / \hbar\}. \end{aligned} \quad (4.10)$$

Correspondingly, the Lorentzian function (the last factor of (4.7)) is replaced by

$$(1 + \eta_{\lambda}) \frac{(\hbar \Gamma_{\lambda 0} / 2) + 2 \mathcal{A}_{\lambda} \{\hbar \omega - (\epsilon_{\lambda 0} + \Delta_{\lambda 0})\}}{\{\hbar \omega - (\epsilon_{\lambda 0} + \Delta_{\lambda 0})\}^2 + (\hbar \Gamma_{\lambda 0} / 2)^2}, \quad (4.11)$$

where

$$\eta_{\lambda} = - \mathcal{P} \int f'(E) / E \cdot dE, \quad (4.12)$$

$$\mathcal{A}_{\lambda} = (\pi/2) f'(0). \quad (4.13)$$

The line shape of (4.11) is asymmetric: the peak position is given by $\hbar \omega_{\max} = (\epsilon_{\lambda 0} + \Delta_{\lambda 0}) + \frac{1}{2} \mathcal{A}_{\lambda} \hbar \Gamma_{\lambda 0}$, the half-value position on the high energy side by $\hbar \omega_{+1/2} = (\epsilon_{\lambda 0} + \Delta_{\lambda 0}) + (\frac{1}{2} + \mathcal{A}_{\lambda}) \hbar \Gamma_{\lambda 0}$, and that on the low energy side by $\hbar \omega_{-1/2} = (\epsilon_{\lambda 0} + \Delta_{\lambda 0}) - (\frac{1}{2} - \mathcal{A}_{\lambda}) \hbar \Gamma_{\lambda 0}$. The degree of asymmetry is thus given by

$$\{(\hbar \omega_{+1/2} + \hbar \omega_{-1/2}) - 2 \hbar \omega_{\max}\} / \hbar \Gamma_{\lambda 0} = \mathcal{A}_{\lambda}. \quad (4.14)$$

In the first approximation as regards $f(E)$, the half-value width is not altered** whereas the peak height suffers the fractional change η_{λ} . As the total area of the λ -peak conserves so far as we neglect the non-diagonal $U(t; \lambda\lambda')$ ($\lambda' \neq \lambda$), the compensating change must occur in the tail part of the absorption band.

§ 5. The strong coupling limit

If one takes the approximation of narrow exciton energy bands, whose exact meaning

* As for the proof of this theorem, see, for example, a work by van Hove.²⁰⁾

** Strictly speaking, $\Gamma_{\lambda 0}$ in the exponential function of (4.10) suffers the fractional change of the first order in $f(E)$, when one takes U_4 into account. However, so far as the product of the peak height and the half-value width is concerned, as will be in § 7, η_{λ} alone is effective for the change.

will be explained later, it is appropriate to expand $\exp[i(\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} \mp \hbar\omega_{\mu\mathbf{w}}) \mp \hbar\tau]$ of (3.19) in a power series of τ when $\lambda_1 = \lambda$, though it is not the case for $\lambda_1 \neq \lambda$. Thus we have

$$\begin{aligned} U_2(t; \lambda\lambda; \mathbf{K})^\dagger &= -\hbar^{-2} \sum_{\lambda_1} \int_0^t (t-\tau) e^{i(\varepsilon_{\lambda\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}}) \tau / \hbar} d\tau \\ &\times [B_{\lambda_1, \lambda\lambda} + \sum_{n=1}^{\infty} (i\tau/\hbar)^n / n! \cdot B_{\lambda_1, \lambda\lambda}^{(n)} \mathbf{K}], \end{aligned} \quad (5.1)$$

where

$$\begin{aligned} B_{\lambda_1, \lambda\lambda}^{(n)} \mathbf{K} &= \sum_{\mu} \sum_{\mathbf{w}} \beta_{\mu\lambda_1\lambda}^* (\mathbf{w}) \beta_{\mu\lambda_1\lambda} (\mathbf{w}) \\ &\times \left\{ (n_{\mu\mathbf{w}} + 1) (\varepsilon_{\lambda_1\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} - \hbar\omega_{\mu\mathbf{w}})^n \right. \\ &\left. + n_{\mu\mathbf{w}} (\varepsilon_{\lambda_1\mathbf{K}} - \varepsilon_{\lambda_1\mathbf{K}+\mathbf{w}} + \hbar\omega_{\mu\mathbf{w}})^n \right\} = B_{\lambda_1, \lambda\lambda}^{(n)*} \mathbf{K}, \\ B_{\lambda_1, \lambda\lambda} &\equiv B_{\lambda_1, \lambda\lambda}^{(0)} \mathbf{K} \text{ (independent of } \mathbf{K}). \end{aligned} \quad (5.2)$$

The ratios of successive coefficients, $B^{(n+1)} / B^{(n)}$, are of the order of $(\hbar/2)$ where $\hbar$ is the breadth of each exciton energy band (phonon energies $\hbar\omega_{\mu\mathbf{w}}$ being neglected).

Consider the term $\lambda_1 = \lambda$ in (5.1) :

$$-\frac{B_{\lambda, \lambda\lambda}}{2\hbar^2} t^2 + \sum_{n=1}^{\infty} \frac{B_{\lambda, \lambda\lambda}^{(n)}}{(n+2)!} \left(\frac{it}{\hbar} \right)^{n+2}, \quad (5.3)$$

and define

$$D_{\lambda}^2 = B_{\lambda, \lambda\lambda}. \quad (5.4)$$

For values of $|t|$, for which the first term of (5.3) is of the order of unity, the n -th term is of the order of $(\hbar/2D)^{n-1} / (n+1)!$. Assuming $\hbar/2 \ll D$, which means that the exciton energy bands are narrow enough, or that the exciton-lattice interaction is strong enough (see (5.4) and (5.2)), let us approximate

$$\begin{aligned} U_0(t; \lambda\lambda; \mathbf{K}) + U_2(t; \lambda\lambda; \mathbf{K})_{\lambda_1=\lambda \text{ only}} + \dots \\ = 1 - \frac{D_{\lambda}^2}{2\hbar^2} t^2 + \dots \approx \exp\left(-\frac{D_{\lambda}^2}{2\hbar^2} t^2\right). \end{aligned} \quad (5.5)$$

After Fourier transformation, we get the absorption coefficient for the λ -th band :

$$A_{\lambda}(\omega) = \frac{4\pi}{3} \frac{\hbar^2 e^2 |\mathbf{g}_{\lambda 0}|^2}{m^2 v_0 c n \omega} \frac{1}{\sqrt{\pi} D_{\lambda}} \exp\left\{-\frac{(\hbar\omega - \varepsilon_{\lambda 0})^2}{2D_{\lambda}^2}\right\}, \quad (5.6)$$

which is of a Gaussian shape with a peak at $\varepsilon_{\lambda 0}$ and a half-value width $H = 2\sqrt{2} (\ln 2) D_{\lambda}$. (We have replaced $\varepsilon_{\lambda\mathbf{K}}$ in (3.15) by $\varepsilon_{\lambda 0}$, because $D \gg \hbar/2$.)

† Here we do not take $\mathbf{K}=0$, because, for the X-ray exciton which is one of the typical cases of strong coupling, $\mathbf{K}$ is not small.

The effects of $\lambda_1 \neq \lambda$ terms in (5.1), as well as those of non-diagonal $U_2(t; \lambda\lambda'; \mathbf{K})$ ($\lambda \neq \lambda'$), will be shown, in § 6, to be of secondary importance if we further assume that $\delta \gg D$, that is, the exciton energy bands are well separated from each other.

That we have taken out only the first term in (5.3) means that we have replaced $H'(t)$ in (3.16) by $H'(0)$. In this approximation, that is, in the limit

$$b/2 \ll D \ll \delta, \quad (5.7)$$

we can calculate all $U_{2m}(t; \lambda\lambda; \mathbf{K})$ ($m=0, 1, 2, \dots$) explicitly, with the result

$$\begin{aligned} \sum_{m=0}^{\infty} U_{2m}(t; \lambda\lambda; \mathbf{K}) &= \sum_{m=0}^{\infty} \frac{1}{(2m)!} \left(\frac{-it}{\hbar} \right)^{2m} \left\{ \frac{(2m)!}{2^m m!} \right\} D_{\lambda}^{2m} \\ &= \exp \left(-\frac{D_{\lambda}^2}{2\hbar^2} t^2 \right), \end{aligned} \quad (5.8)$$

as is easily confirmed by considering the possible combinations of intermediate states in evaluating (3.16). Thus (5.5) proves to be exact in this limit.

That the generating function is written in a closed form (5.8) can be understood from another view-point. When the energy band is very narrow, the "localized exciton" is a sufficiently good eigenstate, and one can consider an adiabatic potential of lattice vibration for this localized exciton state. We can repeat the same mathematical manipulation as was done in the case of a trapped electron.¹⁸⁾ Thus, $H = H_e + H_L + H_{eL}$ is essentially the Hamiltonian for a harmonic oscillator system with equilibrium point displaced due to H_{eL} , the motion of the electronic system being practically freezed. Thus $\exp(-iHt/\hbar)$ in (3.10) can be calculated explicitly, leading to the same result as (5.8), provided phonon energies $\hbar\omega$ are neglected against D , as was done in deriving (5.8). The width D_{λ} of the absorption band is due to the difference in equilibrium positions of lattice before and after excitation.

§ 6. The effect of interband interaction

In the previous two sections we have neglected non-diagonal terms $U_n(t; \lambda\lambda'; \mathbf{K})$ ($\lambda \neq \lambda'$), and further, in the strong coupling case, the terms $\lambda_1 \neq \lambda$ in diagonal $U_n(t; \lambda\lambda; \mathbf{K})$. We now consider the effect of these terms on each absorption band λ .

In the weak coupling case, we proceed in the same way as in § 4. Making use of the formula (4.2), we have

$$\begin{aligned} U_2(t; \lambda\lambda'; 0) &= i\hbar(\varepsilon_{\lambda 0} - \varepsilon_{\lambda' 0})^{-1} [e^{i(\varepsilon_{\lambda 0} - \varepsilon_{\lambda' 0})t/\hbar} \{ \pm (\Gamma_{\lambda\lambda' 0}^*/2) + i(J_{\lambda\lambda' 0}^*/\hbar) \} \\ &\quad - \{ \pm (\Gamma_{\lambda\lambda' 0}/2) + i(J_{\lambda\lambda' 0}/\hbar) \}], \end{aligned} \quad (6.1)$$

where $\pm$ depends on the sign of t , and $\Gamma_{\lambda\lambda' \mathbf{K}}$, $J_{\lambda\lambda' \mathbf{K}}$ are defined as in (4.4) and (4.5), $|\beta_{\mu\lambda_1\lambda}(\mathbf{w})|^2$ being replaced by $\beta_{\mu\lambda_1\lambda}^*(\mathbf{w})\beta_{\mu\lambda_1\lambda'}(\mathbf{w})$. Multiplied with $\exp(-i\varepsilon_{\lambda 0}t/\hbar)$ appearing in (3.15), it is easy to see that the first term in (6.1) contributes to the λ' -peak, whereas the second to the λ -peak. Thus the contribution from

$$F_{\lambda\lambda'}(0) e^{-i\varepsilon_{\lambda 0} t/\hbar} U_2(t; \lambda\lambda'; 0) + F_{\lambda' \lambda}(0) e^{-i\varepsilon_{\lambda' 0} t/\hbar} U_2(t; \lambda'\lambda; 0)$$

of (3.15) to the λ -peak becomes

$$-i\hbar(\varepsilon_{\lambda} - \varepsilon_{\lambda'})^{-1} \{ \pm \operatorname{Re}(F_{\lambda\lambda'} I'_{\lambda\lambda'}) + (2i/\hbar) \operatorname{Re}(F_{\lambda\lambda'} J_{\lambda\lambda'}) \} e^{-i\varepsilon_{\lambda} t/\hbar}, \quad (6.2)$$

where the suffix $\mathbf{K}=0$ has been omitted for brevity.

Adding (6.2) to (4.6) as a correction term, we repeat the same procedure as used in the end of § 4. Finally we get the change of the peak height

$$\eta_{\lambda} = 2 \sum_{\lambda'}^V \operatorname{Re}(F_{\lambda\lambda'} J_{\lambda\lambda'}) / F_{\lambda\lambda}(\varepsilon_{\lambda} - \varepsilon_{\lambda'}), \quad (6.3)$$

and the degree of asymmetry (the definition being given by (4.14))

$$\mathcal{A}_{\lambda} = (1/2) \sum_{\lambda'}^V \operatorname{Re}(F_{\lambda\lambda'} \hbar I'_{\lambda\lambda'}) / \{ F_{\lambda\lambda}(\varepsilon_{\lambda} - \varepsilon_{\lambda'}) \}, \quad (6.4)$$

which are caused by the influence of other bands.

The effect of *interband* interaction represented by η_{λ} and $\mathcal{A}_{\lambda}$ is small if $\hbar\omega_{\lambda\lambda'} \gg J_{\lambda\lambda'}$, $\hbar\Gamma_{\lambda\lambda'}$, that is, if each energy band is well separated and the exciton-phonon interaction is sufficiently weak.

Let us now consider the strong coupling case. As in § 5, we calculate (3.18) or (3.19) by expanding $\exp\{i(\varepsilon_{\lambda'K} - \varepsilon_{\lambda K - m} \pm \hbar\omega_{\lambda\lambda'}) \mp \hbar\}$ in power series, and take out the contribution to the λ -peak in the same way as is described in the above. The calculation being rather tedious, we only mention the result in the following.

Out of the summation

$$\sum_{\lambda'} \sum_{\lambda''} F_{\lambda'\lambda''}(\mathbf{K}) e^{-i\varepsilon_{\lambda'} \mathbf{K} t/\hbar} U_2(t; \lambda'\lambda''; \mathbf{K}),$$

we take the terms which have $\exp(-i\varepsilon_{\lambda'} \mathbf{K} t/\hbar)$ as a principal factor: the contribution to the coefficients from the non-diagonal part ($\lambda' \neq \lambda''$) is given by

$$\begin{aligned} & \sum_{\lambda'}^V \sum_{m=0}^{\infty} (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+1)} 2 \operatorname{Re} [F_{\lambda'\lambda} \{ B_{\lambda'\lambda\lambda}^{(m)} - (-1)^m B_{\lambda,\lambda'\lambda}^{(m)} \}] \\ & + \sum_{\lambda'}^V \sum_{\lambda'' \neq \lambda'}^V \sum_{m=0}^{\infty} (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+1)} [(\varepsilon_{\lambda''} - \varepsilon_{\lambda})^{-1} 2 \operatorname{Re}(F_{\lambda''\lambda} B_{\lambda''\lambda\lambda}^{(m)}) \\ & + (-1)^n (\varepsilon_{\lambda''} - \varepsilon_{\lambda'})^{-1} 2 \operatorname{Re}(F_{\lambda''\lambda'} B_{\lambda,\lambda''\lambda'}^{(m)})] \\ & + \sum_{\lambda'}^V \sum_{n=1}^{\infty} (it/\hbar)^n / n! \cdot \sum_{m=0}^{\infty} (-1)^m (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+1)} 2 \operatorname{Re}(F_{\lambda'\lambda} B_{\lambda,\lambda'\lambda}^{(n-1+m)}) \\ & + \sum_{\lambda'}^V \sum_{\lambda'' \neq \lambda'}^V \sum_{n=1}^{\infty} (it/\hbar)^n / n! \cdot \sum_{m=0}^{\infty} (-1)^m \\ & \times (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-m} (\varepsilon_{\lambda'} - \varepsilon_{\lambda'})^{-1} 2 \operatorname{Re}(F_{\lambda''\lambda'} B_{\lambda,\lambda''\lambda'}^{(n-1+m)}), \end{aligned} \quad (6.5)$$

while the contribution from the diagonal part is written as

$$\sum_{\lambda'}^V F_{\lambda'\lambda'} \sum_{m=0}^{\infty} (-1)^m (m+1) (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+2)} B_{\lambda,\lambda'\lambda'}^{(m)}$$

$$\begin{aligned}
& - \sum_{\lambda'} F_{\lambda\lambda} \sum_{m=0}^{\infty} (m+1) (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+2)} B_{\lambda',\lambda\lambda}^{(m)} \\
& + \sum_{\lambda'} F_{\lambda'\lambda'} (it/\hbar) \sum_{m=0}^{\infty} (-1)^m (m+1) (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+2)} B_{\lambda,\lambda'\lambda'}^{(m+1)} \\
& + \sum_{\lambda'} F_{\lambda\lambda} (it/\hbar) \sum_{m=0}^{\infty} (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+1)} B_{\lambda',\lambda\lambda}^{(m)} \\
& + \sum_{\lambda'} F_{\lambda'\lambda'} \sum_{n=2}^{\infty} (it/\hbar)^n / n! \cdot \sum_{m=0}^{\infty} (-1)^m (m+1) (\varepsilon_{\lambda'} - \varepsilon_{\lambda})^{-(m+2)} B_{\lambda,\lambda'\lambda'}^{(n+m)} \\
& + F_{\lambda\lambda} \sum_{n=2}^{\infty} (it/\hbar)^n / n! \cdot B_{\lambda,\lambda\lambda}^{(n-2)}. \tag{6.6}
\end{aligned}$$

Here the primed summation means that $\lambda' = \lambda$ or $\lambda'' = \lambda$ is to be omitted.

The last term of (6.6) has been discussed in § 5. All the other terms of (6.6) and (6.5) represent the influence of other exciton bands. It is easy to see that these terms are small compared with the last term of (6.6) for values of $t \lesssim \hbar/D_{\lambda}$ (see (5.8)), if the condition (5.7) is satisfied. For instance, a typical term of the last line of (6.5) are smaller than the last term of (6.6) by the order of

$$(D/\hbar)^{m+1} (b/2D)^{m+(n-1)} \quad (m \geq 0, n \geq 1).$$

Thus it is reasonable to regard (5.7) as a sufficient condition for the absorption band to be Gaussian and for the influence of other bands to be negligible, although a complete proof would require the considerations of $U_n(t; \lambda\lambda' \mathbf{K})$ with $n \geq 4$.

The constant terms in (6.5) and (6.6) give the change of the strength (area) of the λ -peak, the terms proportional to $(it/\hbar)$ give the shift, and the terms with $(it/\hbar)^2$ are related with the change of the width, due to the influence of other exciton bands.

§ 7. Further discussions of the theoretical conclusions

In this section we rewrite the conclusions of the previous three sections more explicitly, by making use of appropriate models or approximations in calculating relevant quantities.

(i) Calculation of $P_{\lambda K}$ in the effective mass approximation

This quantity, given by (4.4), is not only related to the width of the absorption band in the weak coupling case, but it is also important in discussing the dynamical behavior of excitons in the vibrating lattice field. It consists of the intraband and interband transitions, of which we here confine ourselves to the former.

Let us take the effective mass approximation (2.2) $\sim$ (2.9), m_e and m_h being assumed to be isotropic. We take the lowest exciton band, and assume that the wave function for the relative motion is of a hydrogenic 1s-type: $\varphi_{1s}(\mathbf{l}) = (\alpha^3/\pi)^{1/2} \exp(-\alpha l)$. Putting (2.16) (2.17) and (2.18) into (4.4), we get, as the contribution of the acoustical mode to the $1s \rightarrow 1s$ scattering (see also ref. 11),

$$\Gamma_{1s, K \rightarrow 1s}(\text{ac.}) = \frac{4m^* v_0 \kappa T}{9\pi \hbar^3 M u^2} (C_v - C_c)^2$$

$$\times \begin{cases} 2w_{ac} & (K^* < w_{ac} - \text{region I}), \\ (K^{*2} + w_{ac}^2)/K^* & (w_{ac} < K^* \leq \alpha, w_0 - \text{region II}), \end{cases} \quad (7.1)$$

$$\quad (7.1')$$

$$\begin{aligned} &= \frac{4m^* v_0 \kappa T}{9\pi \hbar^3 M u^2} \frac{\alpha^2}{K^*} \left(\frac{C_v^2}{3p_h^2} \left\{ 1 - \left(1 + \frac{p_h^2 K^{*2}}{\alpha^2} \right)^{-3} \right\} \right. \\ &+ \frac{C_c^2}{3p_e^2} \left\{ 1 - \left(1 + \frac{p_e^2 K^{*2}}{\alpha^2} \right)^{-1} \right\} - \frac{2C_v C_c}{(p_h^2 - p_e^2)^2} \\ &\times \left[p_h^2 \left\{ 1 - \left(1 + \frac{p_h^2 K^{*2}}{\alpha^2} \right)^{-1} \right\} + p_e^2 \left\{ 1 - \left(1 + \frac{p_e^2 K^{*2}}{\alpha^2} \right)^{-1} \right\} \right. \\ &\left. \left. - \frac{2p_h^2 p_e^2}{p_h^2 - p_e^2} \log \left\{ \frac{1 + (p_h^2 K^{*2}/\alpha^2)}{1 + (p_e^2 K^{*2}/\alpha^2)} \right\} \right] \right) \\ & \quad (w_{ac} \quad K^* - \text{region III}), \end{aligned} \quad (7.1'')$$

where

$$w_{ac} \equiv m^* u / \hbar \ll w_0, \quad (7.2)$$

the former being of the order of 10^6 cm^{-1} while the latter, the Debye cut-off wave-number, of the order of 10^8 cm^{-1} . (7.1) ~ (7.1'') are plotted, as a function of

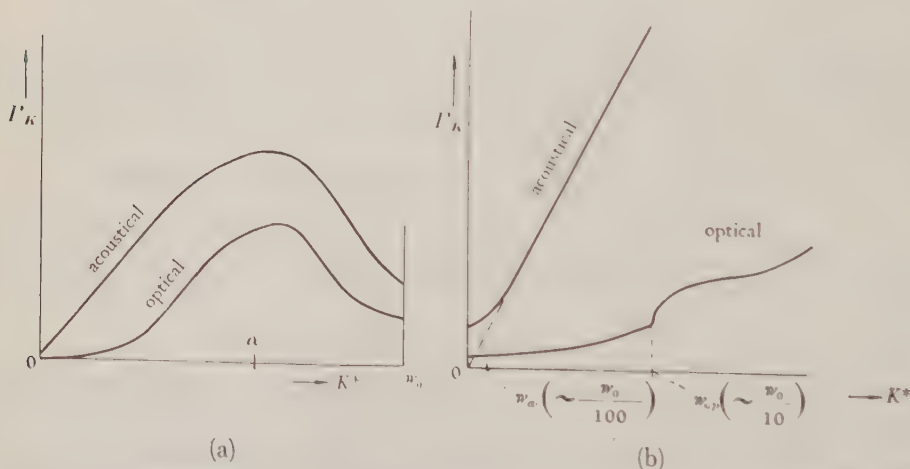


Fig. 2. The scattering probabilities Γ_K of an exciton with wave number $\mathbf{K} = \mathbf{K}_0 + \mathbf{K}^*$, due to acoustical and optical modes, as functions of $\mathbf{K}^*$.

$\mathbf{K}^* (\mathbf{K} = \mathbf{K}_0)$, in Fig. 2. They are valid at high temperatures $T \gtrsim \theta_0(\mathbf{K}^*)$, while at very low temperatures $T \ll \theta_0(\mathbf{K}^*)$, T should be replaced by $\theta_0(\mathbf{K}^*)$ in these formulae. Here the characteristic temperature $\theta_0(\mathbf{K}^*)$ is given by

$$\theta_0(\mathbf{K}^*) = (2\hbar u/3\kappa) \times \begin{cases} (3w_{ac}^2 + K^{*2})/w_{ac} & \text{(Region I),} \\ (K^* + w_{ac})^3/(K^{*2} + w_{ac}^2) & \text{(Region II),} \end{cases} \quad (7.3)$$

$$(7.3')$$

the expression for the region III being omitted as it is rather complicated. It is plotted in Fig. 3 for a typical case. It is of the order of $(\alpha/w_0)\theta_D = \hbar u\alpha/\kappa$ when $K^* \sim w_0$.

In the case of the optical mode we get

$$\Gamma_{1s, \mathbf{K} \rightarrow 1s}(\text{op.}) = \omega e^2 \left(\frac{1}{\kappa_0} - \frac{1}{\kappa} \right) \frac{1}{2} (p_h^2 - p_e^2)^2 \frac{m^*}{\hbar^2 \alpha^4} \times \begin{cases} \bar{n}(2K^{*2} + w_{op}^2) \sqrt{K^{*2} + w_{op}^2} & (0 < K^* < w_{op} \text{—region I'}), \\ [\bar{n}(2K^{*2} + w_{op}^2) \sqrt{K^{*2} + w_{op}^2} + (\bar{n} + 1)(2K^{*2} - w_{op}^2) \sqrt{K^{*2} - w_{op}^2}] & (w_{op} < K^* \leq \alpha, w_0 \text{—region II'}), \end{cases} \quad (7.4)$$

$$(w_{op} < K^* \leq \alpha, w_0 \text{—region II'}), \quad (7.4')$$

where

$$w_{op} \equiv (2m^* \omega/\hbar)^{1/2} \ll w_0, \quad (7.5)$$

the former being of the order of 10^7 cm^{-1} . The expression for the region III': $K^* \gg w_{op}$ has been omitted for brevity (see also ref. 11). These are plotted in Fig. 2 for a typical case.

It is to be noted that for all values of $\mathbf{K}^*$ the contribution of the optical mode is relatively unimportant, as is already stated in § 2. Especially, for small values of K^* , the contribution is quite negligible compared with that of the acoustical mode (see Fig. 2a). Thus, a thermal exciton with $K^* \sim (3m^* \kappa T/\hbar^2)^{1/2}$ is scattered by acoustical vibrations alone. The mean free path l is given by

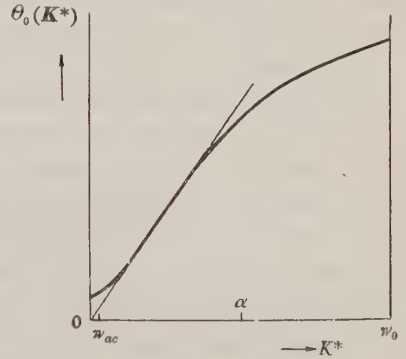


Fig. 3. The characteristic temperature $\theta_0(\mathbf{K}^*)$ for $\Gamma_{1s} \mathbf{K} \rightarrow 1s$ (ac).

$$l^{-1} = \Gamma(\hbar K^*/m^*)^{-1} = \frac{4}{9\pi} \frac{m^{*2} v_0 \kappa T}{\hbar^4 M u^2} (C_v - C_e)^2, \quad (7.6)$$

for values of K^* which are $\gg w_{ac}$ and $\ll \alpha, w_0$, being independent of K^* . It is valid at all temperatures, except at very low temperatures of a few degree (see (7.3')). Moreover, it does not depend on the wave function of the internal motion of the exciton.

In the same way, we can calculate $\Delta_{\lambda \mathbf{K}}$ and D_{λ} , which are related to the peak shift in the weak coupling case and to the half-value width in the strong coupling case, respectively; however the result is rather complicated, and will not be written here.

(ii) A simplified approximation for the overall structure of $f(E)$

The effective mass approximation used in the above has two drawbacks; firstly, it is valid only for the excitons near the extremum of the energy band; secondly it is presumably not a good approximation for the internal motion of the exciton which has a binding energy as large as $1 \sim 2 \text{ eV}$, as is the case for alkali-halide crystals.

As regards the latter situation, it would be more practical, at least in the present stage, to take into account the effect of internal motion by assuming, in (2.17), that

$$q_e(\mathbf{w}; \lambda\lambda) = q_h(\mathbf{w}; \lambda\lambda) = \begin{cases} 1 & \text{when } \mathbf{w} < \mathbf{w}_\lambda^{(e)}, \\ 0 & \text{when } \mathbf{w}_\lambda^{(e)} < \mathbf{w} < \mathbf{w}_0, \end{cases} \quad (7.7)$$

where $(\mathbf{w}_\lambda^{(e)})^{-1}$ is of the order of exciton radius. Then the calculation of D , defined by (5.4) and (5.2) becomes quite simple, the result is written as*

$$D^2 = \frac{4}{9} \frac{C^2}{Mu^2} \left(\frac{\mathbf{w}^{(e)}}{\mathbf{w}_0} \right)^3 \times \begin{cases} \kappa T & T \gtrsim \theta_0, \\ \kappa \theta_0 & T \ll \theta_0, \end{cases} \quad (7.8)$$

where

$$\theta_0 = (3/8) \hbar u \mathbf{w}^{(e)} / \kappa, \quad (7.9)$$

and $C \equiv C_c - C_v$.

As for the first problem, we note that not the local (the neighborhood of the bottom or the top) but rather overall structure of the exciton energy band is important in calculating $f_\lambda(E)$, which was defined by (3.20) and characterizes the main feature of the line shape.

If we confine ourselves to *intragand* effect, and moreover neglect phonon energies in (3.20), $f_\lambda(E)$ is different from zero in the interval $(\epsilon_{\lambda 0} - \epsilon_{\lambda 10}, \epsilon_{\lambda 10} - \epsilon_{\lambda 20})$, where $\epsilon_{\lambda 0}$ and $\epsilon_{\lambda 10}$ means the energies of the bottom and the top of the energy band. Further, it is easily confirmed that at the both ends of the interval $f(E)$ tends to zero as $|E - (\epsilon_{\lambda 10} - \epsilon_{\lambda 0})|^{1/2}$ or $\{(\epsilon_{\lambda 10} - \epsilon_{\lambda 0}) - E\}^{1/2}$. If most part of the λ -energy band lies on the high energy side of $\epsilon_{\lambda 0}$, it is rather plausible to suppose that the peak shift Δ is negative according to (4.5), and that the asymmetry $\mathcal{A}$ is positive due to (4.13).

In order to take into account these situations in a simplest way we assume the following functional form for $f(E)$:

$$f_\lambda(E) = \frac{s_\lambda}{\pi} \left\{ \left(\frac{b_\lambda}{2} \right)^2 - \left(E - \frac{b_\lambda}{2} p_\lambda \right)^2 \right\}^{1/2} \quad (-1 \leq p_\lambda \leq +1), \quad (7.10)$$

where b_λ is the breadth of the λ -energy band, and p_λ is a parameter representing the position of $\epsilon_{\lambda 0}$ in the whole energy band. $p = +1 (-1)$ corresponds to the case that $\mathbf{K} = 0$ is at the bottom (top) of the band. The normalization constant s_λ is determined by considering that the integral of $f_\lambda(E)$ is equal to D_λ^2 according to (3.20) and (5.2); that is:

$$s_\lambda = 8D_\lambda^2 / b_\lambda^2. \quad (7.11)$$

Note that a large s corresponds to a *large* coupling constant, to *high* temperatures or to a *narrow* energy band, as is easily seen from (7.8) and (7.11). In the following, we shall omit the suffix λ so far as the *intragand* effect is concerned.

Making use of (7.10) we can calculate the quantities given by (4.4), (4.5), (4.12) and (4.13); the results are as follows:

$$H = \hbar \Gamma = s \sqrt{1 - p^2} b, \quad (7.12)$$

$$J = -(sp/2)b, \quad (7.13)$$

$$\mathcal{L} = (sp/2)/\sqrt{1 - p^2}, \quad (7.14)$$

$$\eta = s. \quad (7.15)$$

(iii) Criterion for the classification into Lorentzian and Gaussian cases

The power series (5.1) is calculated, with the use of (7.10) and (7.11), as

$$U_2 = -\frac{1}{2} D^2 \left(\frac{t}{\hbar} \right)^2 + \frac{1}{12} i p D^2 b \left(\frac{t}{\hbar} \right)^3 + \frac{1}{96} \left(p^2 + \frac{1}{4} \right) D^2 b^2 \left(\frac{t}{\hbar} \right)^4 + \dots \quad (7.16)$$

If $s \gg 1$, we can neglect all but the first term in (7.16), as well as in $U_4, U_6, \dots$,

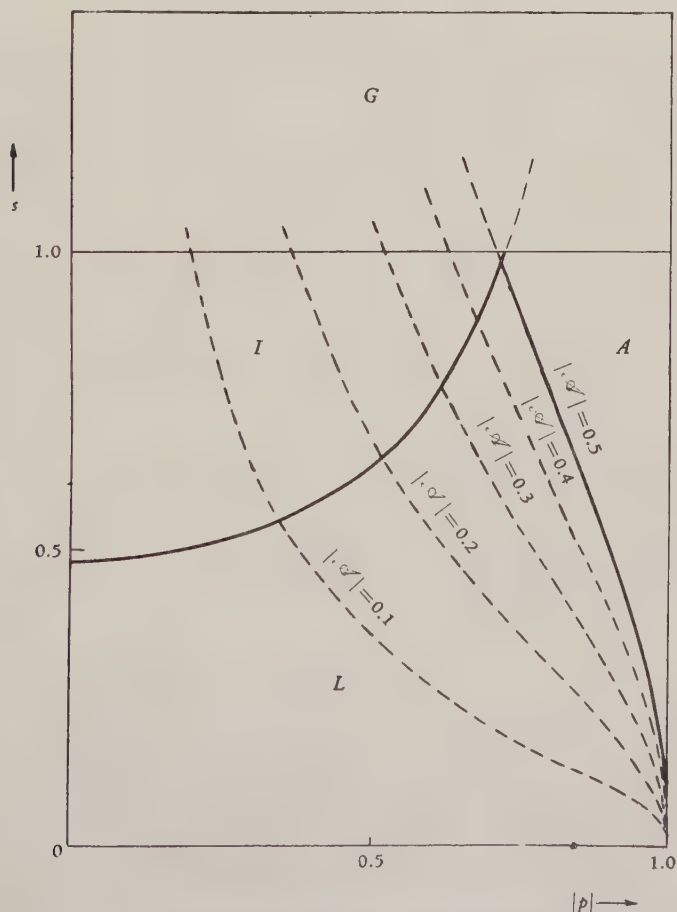


Fig. 4. The classification into Gaussian, Lorentzian, Asymmetric and Intermediate cases according to values of p and s .

and therefore get (5.8), which leads to a Gaussian line shape.

Next we introduce the ratio of the half-value width formula for the Lorentzian case to that for the Gaussian case :

$$r \equiv \frac{\hbar \Gamma_{\lambda 0}}{2\sqrt{2} (\ln 2) D_{\lambda}} = \frac{1}{\ln 2} \sqrt{1-p^2} \sqrt{s}. \quad (7.17)$$

According as $r \gg 1$ or $r \ll 1$, the dynamical region (5.5) or the stochastic region (4.6) becomes more important than the other. In order that the Lorentzian case is realized, not only the relation $r \ll 1$, but also (4.8) should be satisfied. In the present approximation, $\tau_c(0)$ defined by (4.1) is calculated as*

$$\tau_c(0) = \{2|p|/(1-p^2)\} \hbar/b, \quad (7.18)$$

and (4.8) is rewritten as follows :

$$s|p|/\sqrt{1-p^2} = 2|\mathcal{A}| \ll 1. \quad (7.19)$$

In Fig. 4 we divide the $(|p|, s)$ plane into several regions according to the above discussions. The region *G* (Gaussian) is defined by $s > 1$, whereas *L* (Lorentzian) is determined by $r < 1$ and $|\mathcal{A}| < 1/2$. We denote by *A* (asymmetric) the region where $s < 1$ and $|\mathcal{A}| > 1/2$, and the remaining region will be called *I* (intermediate).

(iv) *Temperature dependence and the effect of lattice imperfections.*

In the above discussions we have considered the dynamical vibrations of the lattice. When there are any types of lattice imperfections such as dislocations, vacancies, interstitial atoms or impurities, a static displacement of the lattice is brought about. The expectation values $b_{\mu\nu}^*$, $\bar{b}_{\mu\nu}$ are generally not equal to zero. If, how-

ever, the imperfections are distributed at random, as is presumably the case in actual crystals, the linear effect of b almost cancels out, and we have only to replace $n_{\mu\nu} = b_{\mu\nu}^* b_{\mu\nu} \propto T (T \gtrsim \theta_D)$ by a suitable quantity which is proportional to the density of imperfections. Thus the effect of increasing imperfections are qualitatively the same as

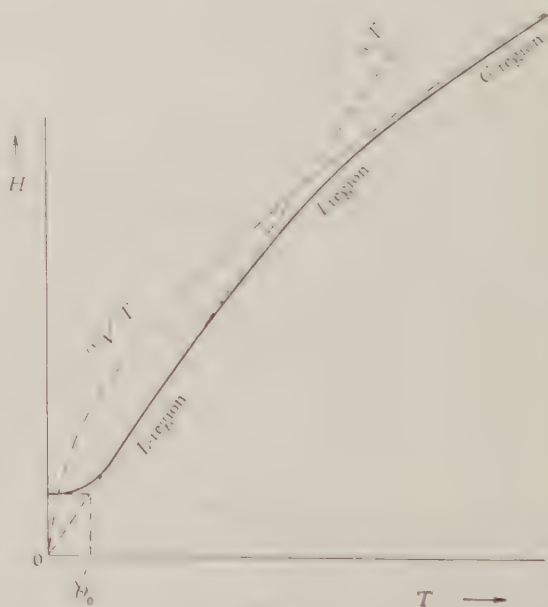


Fig. 5. A typical temperature dependence of the half-value width H expected from theory.

* We use $\tau_c(0)$ instead of $\tau_c(E)$, because the value near $E=0$ is the most important in using the δ -function approximation (4.2).

that of raising temperatures. In the following statements, which concern the *temperature* dependence of the line-shape, the word "absolute temperature" can be replaced, when one deals with the dependence on *imperfection*, by "the density of imperfections" with a suitable proportionality constant, without any other substantial modifications.

As we have seen in (iii), the exciton absorption band is of a Gaussian shape when the exciton-lattice coupling is strong or the exciton energy band is narrow (corresponding to large effective mass), while it is Lorentzian in the opposite limit. If these quantities are in suitable ranges, s increases from a value $s < 1$ at $T = 0^\circ\text{K}$ to values > 1 at high temperatures (see (7.11) and (7.8)); that is, the line shape is Lorentzian at low temperatures and tends to Gaussian as the temperature is raised. If $\epsilon_{\lambda 0}$ is near the bottom or the top of the energy band ($1 - |p| \ll 1$), the line shape is strongly asymmetric in a rather wide-spread intermediate range of s (see Fig. 4).

In the region L , the half-value width H is proportional to T except at low temperatures ($T \lesssim \theta_0$, see (7.12), (7.11) and (7.8)), while it is proportional to $\sqrt{T}$ in G (see Fig. 5).

The *interband* interaction becomes important when other exciton energy bands lie close to the band we are considering. For example, the peak shift (being proportional to T) due to the *intraband* effect is given by (7.13), and it is negative or positive according as $\epsilon_{\lambda 0}$ is near the bottom or the top of the band, while the contribution of the *interband* effect is given by

$$\Delta_\lambda \approx \sum_{\lambda'} \frac{B_{\lambda', \lambda \lambda}}{\epsilon_{\lambda 0} - \epsilon_{\lambda' 0}} \sim O\left(\frac{D^2}{\delta}\right) \quad (7.20)$$

according to (4.5), which is negative for the lowest exciton band. In the region G , the contribution of *intraband* effect to the shift is small, whereas the *interband* transition causes a shift given by

$$\Delta_\lambda' \approx \sum_{\lambda'} \frac{1}{\epsilon_{\lambda 0} - \epsilon_{\lambda' 0}} \left\{ B_{\lambda', \lambda \lambda} + \frac{\text{Re}(F_{\lambda' \lambda} B_{\lambda, \lambda' \lambda})}{F_{\lambda \lambda}} \right\} \sim O\left(\frac{D^2}{\delta}\right), \quad (7.21)$$

if we take the terms with the lowest order in (b/δ) , out of the coefficients of $(-it/b)$ in (6.5) and (6.6). In the same approximation the dispersion in the region G is given by

$$D_\lambda^2 - \Delta_\lambda'^2. \quad (7.22)$$

The first term of (7.22) is proportional to T while the second is to T^2 . It is possible that as temperature rises the half-value width tends to saturate or even to decrease, although in such regions, the peak separation becomes very poor due to $D \sim \delta$.

As for the asymmetry in the region L , there is a contribution from the *interband* effect given by (6.4), besides the *intraband* effect (7.14). It is to be noted that both are proportional to T . If two exciton bands lie very close to each other, and if the *interband* contribution is dominant as regards δ , both absorption peaks are expected to have slower decents towards the outside (Fig. 6a) or the inside (Fig. 6b) according as

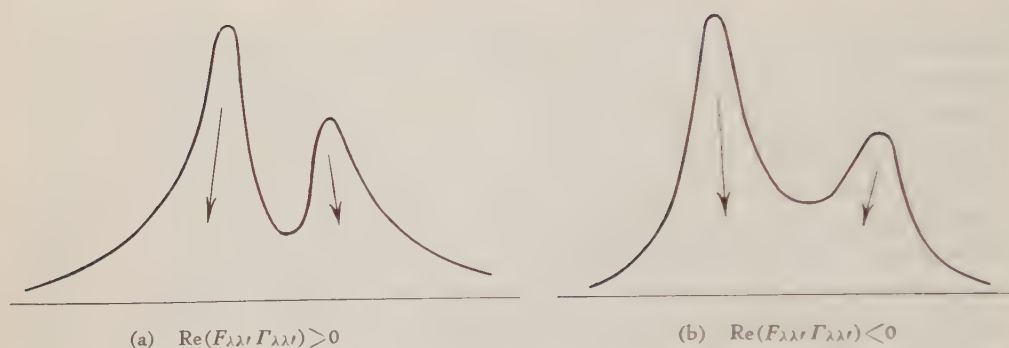


Fig. 6. The interband effect on the asymmetries of adjacent peaks.

$\text{Re}(F_{\lambda\lambda'}, F_{\lambda\lambda'}) \leq 0$, the smaller peak being distorted more strikingly than the larger one.

In the region L , the product of the peak height and the half-value width varies as $1 + \gamma$, where γ is proportional to T (at $T \lesssim T_1$). The contribution from the *intra*-band transition is given by (7.15) and is positive,* whereas the *inter*-band effect is given by (6.3). In the region G , γ is mainly due to the *inter*-band effect. In the lowest order of (b/δ) , it is given by

$$\eta_\lambda = \sum_{\lambda'} \frac{B_{\lambda', \lambda\lambda}}{(\epsilon_{\lambda 0} - \epsilon_{\lambda' 0})^2} \frac{-F_{\lambda\lambda} + F_{\lambda'\lambda'}}{F_{\lambda\lambda}} + \sum_{\lambda'} \frac{2}{(\epsilon_{\lambda 0} - \epsilon_{\lambda' 0})^2} \frac{\text{Re}\{F_{\lambda'\lambda}(B_{\lambda', \lambda\lambda} - B_{\lambda, \lambda'\lambda})\}}{F_{\lambda\lambda}} \quad (7.23)$$

(see (6.5) and (6.6)), and is proportional to T .

(v) Physical meanings of the criterion

Let us consider the meaning of $\tau_c(0)$ defined by (4.1). According to (4.2) and (4.3), the probability that an exciton has suffered a collision by a phonon is proportional to t only if $|t| \gg \tau_c$; τ_c is considered to be a minimum duration time of collision: if we imagine a wave packet of an exciton which collides with a wave packet of a phonon and is then scattered, the collision duration time is of the order of τ_c in the most favorable cases (that is, for appropriate forms of the initial wave packets). Thus the condition (4.8) for the Lorentzian case means that the time between successive collisions is large compared with the collision duration. This is the well-known condition for the validity of the usual transport equations, and was discussed by Peierls¹⁷ for the case of metallic conductivity, by Seitz^{18,19} for the case of semiconductors, and has recently been extended to general case by van Hove.²⁰

It is instructive to compare the division in Fig. 4 with the "polaron" problem.¹⁶⁾ The region L corresponds to the weak-coupling case, where the usual perturbation theoretical calculation is valid, while the region G corresponds to the strong coupling case where

* That it is positive seems to be very probable, irrespective of the approximation (7.10). For, in (4.12), $f'(E)$ is positive (negative) near the bottom (the top) of the band, where E is negative (positive).

the so-called self-trapped electron is a good approximation. The region A corresponds to a slow electron (note that $1 - |p| \ll 1$) in the intermediate coupling case whose exact treatment is rather difficult. In our case, too, it would be necessary to take into account the cloud effect suitably, in order to discuss the line shape for the region A more elaborately.

The situation in the Lorentzian case is analogous to the motional or exchange narrowing effects of magnetic resonances.⁽²¹⁾ Thus, excitation energy ($\epsilon_{\lambda 0}$), kinetic energy of an exciton ($\epsilon_{\lambda K} - \epsilon_{\lambda 0}$) and exciton-lattice interaction $H_{e/l}$ of our case correspond to Zeeman energy, exchange coupling and dipolar interaction, respectively, of the magnetic case.

§ 8. Comparison with experimental results

We now compare the theoretical conclusions stated in the previous section with several experimental data available at present.

(i) Analysis of Fesefeldt's⁽²⁴⁾ and Martienssen's⁽²⁵⁾ data shows that at low and room temperatures, the first exciton absorption bands of KI and RbBr crystals are Lorentzian in the main, while it approaches the Gaussian shape at high temperatures, as is expected from theory (see § 7 (iv)). Other alkali-halides seem to show the same tendency, though not so clearly as in KI and RbBr.

According to Tutihasi's⁽²⁶⁾ data on AgCl crystal, the absorption curve on the low energy side of the first peak, at $T = -184^\circ\text{C}$, is in excellent agreement with a Lorentzian curve, with half-value width $H = 0.177$ eV. On the high energy side, overlaps with other bands prevent the analysis.

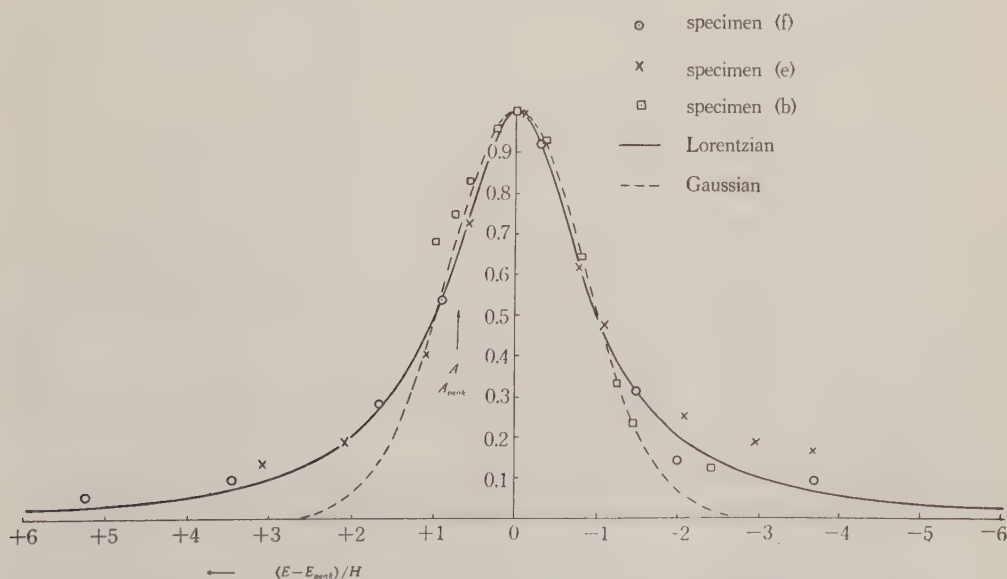


Fig. 7. The absorption curves for the first peak of KI (containing 10 mol % of KF) measured by Fischer. The peak height and the half-value width are reduced to unity for each specimen.

Table 1. The results of analysis of Fischer's data on the first absorption peak of KI crystals containing 10 mol % of KF.

specimen	peak position	peak height	half-value width H	line shape	asymmetry $\mathcal{A}$	area
(f)	5.844 eV	2.16	0.067 eV	L	very small	0.178
(e)	5.840	1.40	0.115	L	-0.08	0.198
(d)	5.795	0.674	0.37	(L)	-0.30	0.305
(c)	5.63					
(b)	5.51	0.467	0.42	G		0.196
(a)	5.48	0.434	0.40	G		0.174

Fischer²⁷⁾ measured, at $T=20^\circ\text{K}$, the absorption coefficients of a number of KI (containing 10 mol % of KF*) films with different preliminary heat treatments. The higher the temperature is maintained or the longer the treatment is continued, the less will be the crystal imperfections. In his specimens (f) and (e), which are considered to be the most perfect ones, the first peak is of a Lorentzian shape with relatively small width, while the specimen (b) and (a) which must have high densities of imperfections show nearly Gaussian shapes with large widths, as is shown in Fig. 7 and Tab. 1. These results again confirm the theoretical expectation (see § 7 (iv)).

In Fig. 8, we plot the half-value widths of the first peaks of KI and RbBr, as measured by Fesefeldt, Fischer and Martienssen at various temperatures. The temperature dependences are in qualitative agreement with the curve of Fig. 5, showing a tendency of bending downward from the linear curves $H \propto T$ (extrapolated

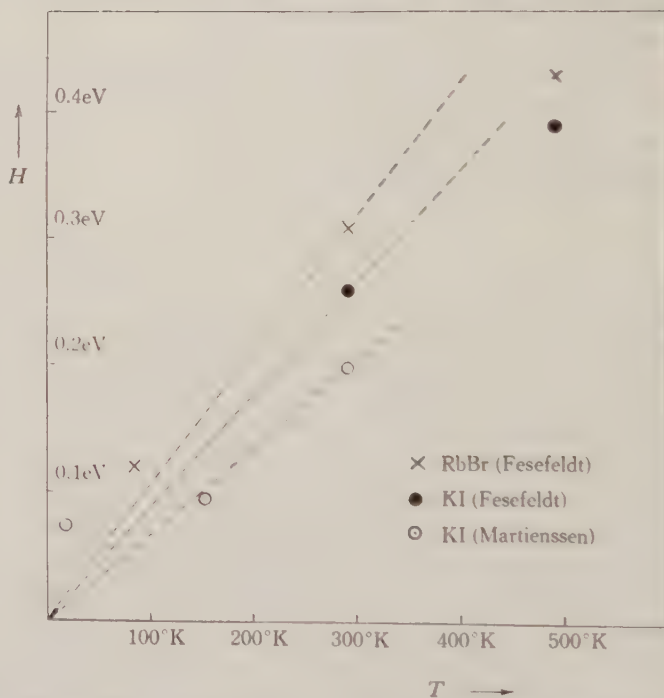


Fig. 8. The observed half-value widths H of the first peaks of RbBr and KI at various temperatures (after Fesefeldt and Martienssen).

* Fischer carried out the experiments on KI containing various amounts of KF. Here we confine ourselves to his specimens containing 10 mole % KF, because his data are most detailed for these, and in addition, the absorption curves seem to be almost the same as in pure KI specimens.

from room temperature values), at high temperatures where the absorption bands are, in fact, Gaussian. The reason for the discrepancy between Fesefeldt's and Martienssen's data is not clear, but it might be due to some kinds of crystal imperfections contained in the former experiment.

(ii) We now proceed to somewhat detailed analysis of Fischer's data on KI. The results of analysis of the first absorption peak are shown in Tab. 1 and Fig. 9. In the first column of Tab. 1, the specimens are arranged in the order of increasing imperfections. We can take the peak shift as a measure for the imperfection density because of (7.13), (7.20) and (7.21) (all of these quantities are proportional to T in the case of temperature variation), though the proportionality constant in the region L is different from that in the region G . In the last column the area defined by $\text{const.} \times (\text{peak height}) \times (\text{half-value width})$ are shown. In the L region, the constant is taken to be $\sqrt{\pi} \ln 2$ times of that in the G region (compare (4.7) and (5.6)).

In the Lorentzian region, H , $\mathcal{A}$, η and shift are expected to be proportional to each other according to (iv) of § 7. This relation is approximately satisfied for the specimens (f), (e) and (d), as is seen from Fig. 9. Making use of the values of H for (f) and (e), the area for the ideal crystal (which means that $H=0$, and is physically not attainable because of zero-point vibration) is extrapolated to be 0.150. For the specimen (e), therefore, we have

$\eta = (0.198 - 0.150)/0.150 = 0.32$, while $\mathcal{A} = -0.08$. Substituting these in (7.14) and (7.15) we have $p = -0.45$, and further comparing (7.12) with the experimental value for (e), we get $b = 0.40$ eV. The peak shift between (f) and (e) is estimated, by (7.13), to be $\Delta = +0.012$ eV whereas the observed value is $\Delta = -0.004$ eV. This discrepancy would be mainly due to the interband effect (7.20), which is certainly negative for the first exciton band.

In the Gaussian region, the peak separation is rather poor, and we have analysed the absorption curve only on the low energy side; the values of H for (b) and (a) were obtained by assuming the sym-

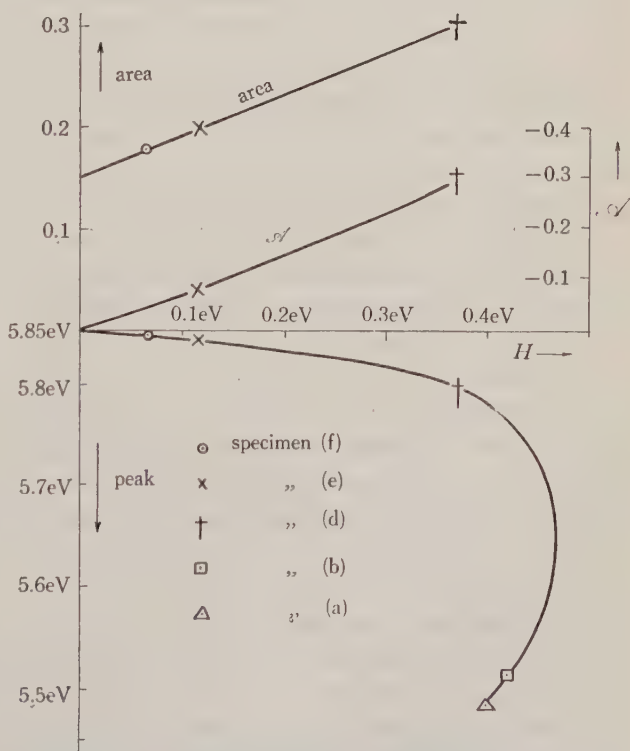


Fig. 9. The area, the asymmetry $\mathcal{A}$ and the peak position as functions of the half-value width H (see Table 1).

metry of the curve, though this is rather doubtful. The saturating or decreasing tendency of H , as the imperfection increases, is, however, well established from this data, and this is in accordance with the theoretical result (7.22). The second exciton peak of KI is separated from the first peak by $\delta \sim 0.5$ eV. We can write the shift of the first peak as $J' = -\nu D^2/\delta$ in view of (7.21) and (5.4), where $\nu (>0)$ is a dimensionless quantity of the order unity. Consequently we get $H \sim 2(D^2 - J'^2)^{1/2} = 2\{- (\delta/\nu) J' - J'^2\}^{1/2}$, and the maximum of H is to be realized at $J'(m) = -\delta/2\nu$ with $H(m) = \delta/\nu$. From Fig. 9 we estimate $H(m) \sim 0.47$ eV and $J'(m) \sim -0.20$ eV, though with some ambiguity. The relation $H(m) = -2J'(m)$ is approximately satisfied. On the other hand we have $D(m) = H(m)/\sqrt{2} \sim 0.33$ eV, and according to (7.11), $s(m) \sim 5$, the result which is consistent with our assumption that this neighbourhood is well in the region G.

(iii) Let us now compare the observed and calculated half-value widths. According to Martienssen's data, the first peak of KI shifts to low energy side by 0.10 eV and the half-value width increases by 0.10 eV as the temperature is raised from 155°K to 293°K. According to Fischer's experiment (Tab. 1), the ratio of the peak shift to the increment of H is $1/12$ for (f) - (e) and $1/6$ for (f) - (d). Thus the most part (~ 0.09 eV) of the temperature shift of the peak is considered to be due to thermal expansion, the remaining part (~ 0.01 eV) being due to the dynamical lattice vibrations (self-energy). Making use of thermal expansion coefficient (linear) $0.4 \cdot 10^{-4}$ deg $^{-1}$, we estimate the deformation potential: $E_1 = -0.09$ eV / $(3 \times 0.4 \times 10^{-4} \times 138) = -5.4$ eV, $C = -(3/2) \times E_1 = 8.1$ eV. If we take the effective mass approximation, this C corresponds to $C_c - C_v$, because the exciton energy band shifts by $E_{1c}J - E_{1v}J$ when the conduction band shifts by $E_{1c}J$ as a whole and the valence band by $E_{1v}J$ (Here J means the dilation).

In this connection it is to be noted that Kawamura¹ has calculated the deformation potential for the conduction band of KCl crystal by the cellular method with result $E_{1c} = -5.4$ eV. It would presumably be smaller for KI crystal. On the other hand, E_{1v} would be of the order of $+Mc^2/3a \sim 2.4$ eV for KI (M : Madelung constant, a : lattice constant) because each of valence band electrons is considered to be fairly localized on a halogen ion. Thus the value $E_1 = -5.4$ eV can be reasonably explained.

Comparing (7.12), (7.11) and (7.8) with Martienssen's data $H = 0.20$ eV at $T = 293^\circ\text{K}$, and inserting $C = 8.1$ eV, $M\kappa^2/c_v - c_m = 0.25 \cdot 10^{12}$ dyne cm $^{-2}$ (we follow the procedure due to Bardeen and Shockley^{1,2} in evaluating c_m ; as for the elastic constants see ref. (29)), $b = 0.40$ eV and $p = -0.45$, we get $n^{(1)}_1 = 0.62$. This means that the radius of the exciton is slightly larger than the lattice constant, which seems plausible in the case of alkali-halides.

According to (7.8), the low temperature value of H should be (θ_0/T) times the value at a high temperature T (still in the L region). Comparing Fischer's data $H = 0.067$ eV (the specimen (f) at 20 K) with Martienssen's data at $T = 293$ K stated above, we get $\theta_0 = 99^\circ\text{K}$. On the other hand, the Debye temperature $\theta_D = \hbar\omega_D/k$ is estimated to be 190°K . Now, θ_0 must be smaller than $\theta_D/2$ according to the general theory. If we use (7.9) θ_0 is estimated to be 40°K . Although this estimation has

only qualitative meaning, the observed H at 20°K seems too large to be explained by the zero-point lattice vibration alone. This discrepancy is presumably due to a small amount of imperfections frozen in, in an inevitable way, on cooling the crystal, the fractional contribution of which is larger for lower temperatures. We must also add that, of Fischer's data, we are analysing only those specimens which contains 10 mol % of KF.

(iv) In the above, we have neglected the *interband* effect (except in the Gaussian case). This effect is presumably not small, as is pointed out in (ii) in connection with the peak shift, and consequently the estimated values of b and p are of only qualitative meaning. Moreover, the true width of the energy band might be larger than b , because the latter is the width of that part of the energy band which is connected with the point $\mathbf{K}=0$ through the transition coefficient $\beta(\mathbf{K})$ of appreciable magnitude. b may be much smaller than the true width of the energy band if the exciton radius is large, while they do not differ very much for the case of alkali-halides.

On the other hand, the band bottom $\epsilon_{\lambda b}$ is estimated, according to (ii), to lie $(1-p)b/2 = 0.29$ eV below $\epsilon_{\lambda 0}$. This is consistent with the observed value 0.32 eV for the energy difference between the first peak and the β -absorption peak.³⁰⁾ The latter corresponds to the creation of an exciton which is trapped in the neighbourhood of the F -center, and the required energy must be smaller than $\epsilon_{\lambda b}$ by a trapping energy.

Here we should like to refer also to Howland's³¹⁾ calculation on the energy band structure of KCl, according to which the valence band is fairly narrow (~ 1 eV) and the uppermost branch has a maximum on a (011) direction nearly midway between the center and the edge of the first Brillouin zone. Making use of his result, and assuming that the bottom of the conduction band is at $\mathbf{K}=0$ with effective mass equal to the true electron mass, the procedure described in (2.2) $\sim$ (2.9) leads to an exciton energy band which is fairly narrow and whose bottom is coincident with the top of the valence band in $\mathbf{K}$ -space. The situation would be qualitatively the same for KI (apart from the large spin-orbit splitting of the valence band³²⁾). This rather speculative consideration is consistent with the result of the above analysis.

(v) According to Martienssen,²⁵⁾ the first exciton peak of CsI is followed by the second and third peaks with rather small gaps, and shows, at the same time, a strong asymmetry ($\mathcal{A} = -0.23$ even at 20°K ; compare with the specimen (f) of KI in Tab. (1). It is very probable that this strong asymmetry is largely due to the interband effect. In the data of Philipp and Taft,³³⁾ the temperature dependence of the separation between the first peak and the other two peaks is well expressed by the formula $\alpha + \gamma T$ where $\alpha = 0.21$ eV and $\gamma = 6.4 \cdot 10^{-4}$ eV/K $^\circ$. These values of $\mathcal{A}$ and γ are reasonably explained by (6.6) and (7.20) if we assume that the *interband* exciton-lattice coupling constant is as large as the *intraband* one.

(vi) In Cu_2O crystal, three hydrogenlike series of absorption lines are observed,^{34) 35)} which are interpreted by Gross and Nikitine to be due to excitons. Each line has a very small width H , of the order of 10^{-3} eV at most.³⁵⁾ This might be partly due to the large radius³⁶⁾ of the exciton which makes $(w^{(e)}/w_0)^3$ of (7.8) fairly small, and partly

due to the smallness of C itself (note that $H \propto C^2$). In fact, the temperature shifts of the series limits⁽¹¹⁾ are as small as one tenth of that of the first peak in KI, thus leading to a small deformation potential.

(vii) In the case of an X-ray exciton, the hole corresponds to the innermost shell of an atom, and the effective mass m_h is very large. In this case, the dipole-dipole interaction of the Heller-Marcus⁽¹²⁾ type might be more important in determining the effective mass m^* of the exciton; nevertheless m^* would be large unless the oscillator strength for the transition is as large as ~ 1 . Thus we expect that the absorption peak corresponding to an X-ray exciton is of a Gaussian type for any temperature.

The experimental data for KCl due to Kiyono,⁽¹³⁾ as well as that due to Trischka⁽¹⁴⁾ seem to support this conclusion, as has also been noted by Parratt and Jossem,⁽¹⁵⁾ although a quantitative analysis of the line shape is rather difficult in the present stage of X-ray spectroscopy. The observed half-value widths (2~3 eV), on the other hand, seem to be too large to be explained by the exciton lattice interaction alone.

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Low Energy Electron-Hydrogen Scattering

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The effective range theory is developed for electron-hydrogen scattering. The scattering length a_s and the effective range r_{0s} of the singlet state are determined by making use of the accurate solution of the H^- ion state, as

$$a_s = 7.03, \quad r_{0s} = 3.37 \quad (\text{in atomic unit}).$$

The scattering length a_t and the effective range r_{0t} of the triplet state are calculated from the zero energy solution by a variation-perturbation method. The results are $a_t = 2.34$, $r_{0t} = 1.29$.

§ 1. Introduction

The scattering of an electron by a hydrogen atom is the simplest and the most fundamental problem among electron-atom scatterings. Apart from the direct application of the result to the exploration of the physical condition of celestial bodies, to the researches of discharge phenomena and so on, it has an important theoretical significance as a test of various approximations used in the calculations in more complicated collision problems pertaining to a complex atom.

The method of calculation for the problem of electron-hydrogen scattering at low energies has been improved by many authors.¹⁾ The Born and distorted wave approximation in a central field of a hydrogen atom gave a rather poor result, for one finds the same cross-section for both the singlet and the triplet states, and also the zero phase-shift for the zero energy limit. The solution of the Hartree-Fock type equation including the exchange effect was obtained accurately by a numerical method.²⁾ Subsequent calculations³⁾ taking the polarization into account showed that the Hartree-Fock approximation gives a fairly good result, especially for the triplet state, but a more refined calculation is needed for the singlet state.

A powerful method for treating a low energy scattering, so-called the effective range theory, was put forward⁴⁾ by Schwinger and Bethe for the nucleon-nucleon scattering, according to which the scattering process is described completely by two quantities—the scattering length a and the effective range r_0 . These quantities are calculated from the wave-function of the state for the zero energy of the incident particle, or by the function of the bound state if the system has a stable bound state with small binding energy such as the deuteron-state for two nucleons. In the case of electron-hydrogen scattering, there also exists a H^- state with a very small affinity, and its state function is calculated quite accurately by the variational method due to Hylleraas.⁵⁾ We shall

find a_s, r_{0s} for the singlet state using this function ψ_{H^-} (actually using Hart-Herzberg function) of the ion state. The values of a_s, r_{0s} obtained are estimated to be very accurate, because the binding energy (affinity) of H^- is very small (~ 0.028) compared with the kinetic energy of the electron inside the Bohr radius, and also because of the reliability of the H^- -function.

For the triplet state, no such handy function exists, so that we have to construct the wave function of the zero energy state to find a_t, r_{0t} . This function is calculated together with that for the singlet state by a variation-perturbation method which is, in a sense, a mixed use of both the variational method for Hartree-Fock and the second Born approximation, and provides improvements on them.

§ 2 recapitulates the results of calculations hitherto obtained, from the standpoint of the effective range theory, and gives the values of a_s, r_{0s} determined from the function of the negative ion state. In § 3 the variation-perturbation method is described to find a and r_0 from the solution of the zero energy state. § 4 contains the summary and the conclusion.

§ 2. Effective range theory

The Schrödinger equation for the system of a hydrogen atom and an electron is, in atomic units,

$$\left\{ \frac{\Delta_1}{2} + \frac{\Delta_2}{2} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} + E \right\} \psi(\mathbf{r}_1, \mathbf{r}_2) = 0. \quad (1)$$

The atomic electron in a hydrogen atom in the ground state is described by a function $\phi(r)$ which satisfies

$$\left\{ \frac{\Delta}{2} + \frac{1}{r} - \frac{1}{2} \right\} \phi(r) = 0, \quad (2)$$

$$\int \phi(r)^2 d\mathbf{r} = 1,$$

so that

$$\phi(r) = e^{-r}/\sqrt{\pi}.$$

We shall normalize the function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &\rightarrow \phi(r_1) \frac{\sin(kr_2 + \delta_{\pm})}{r_2 \sin \delta_{\pm}} && \text{for } r_2 \rightarrow \infty \\ &\rightarrow \pm \phi(r_2) \frac{\sin(kr_1 + \delta_{\pm})}{r_1 \sin \delta_{\pm}} && \text{for } r_1 \rightarrow \infty, \end{aligned} \quad (3)$$

where $\pm$ correspond to the singlet and the triplet states respectively. The total cross-section is given by

$$\sigma = \frac{1}{4} \sigma_+ + \frac{3}{4} \sigma_-, \quad \sigma_{\pm} = \frac{4\pi}{k^2 (1 + \cot^2 \delta_{\pm})}. \quad (4)$$

To express this cross-section in terms of the quantities arising in the effective range theory, the following function, which is equal to the asymptotic form of $\psi(\mathbf{r}_1, \mathbf{r}_2)$, is introduced :

$$u(\mathbf{r}_1, \mathbf{r}_2) \equiv \phi(r_1) \frac{\sin(kr_2 + \delta_\pm)}{r_2 \sin \delta_\pm} \pm \phi(r_2) \frac{\sin(kr_1 + \delta_\pm)}{r_1 \sin \delta_\pm}. \quad (5)$$

Then, following the procedure taken by Bethe¹⁾ in his paper, it is found that

$$\begin{aligned} k_\alpha \cot \delta_\alpha - k_\beta \cot \delta_\beta &= \frac{(k_\alpha^2 - k_\beta^2)}{8\pi} \int_0^\infty (u_\beta u_\alpha - \psi_\beta \psi_\alpha) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\pm (1/2\pi) G(k_\alpha, \delta_\alpha) \{F(k_\beta, \delta_\beta) - 2\pi\phi(0)\} \\ &\mp (1/2\pi) G(k_\beta, \delta_\beta) \{F(k_\alpha, \delta_\alpha) - 2\pi\phi(0)\}, \end{aligned} \quad (6)$$

where the extra terms

$$F(k, \delta) \equiv \int_0^\infty \phi(r) \frac{\sin(kr + \delta)}{r^2 \sin \delta} d\mathbf{r}, \quad G(k, \delta) \equiv \int_0^\infty \phi(r) \frac{\sin(kr + \delta)}{r \sin \delta} d\mathbf{r}$$

arise from the exchange.

Putting $k_\beta = 0$, and expanding according to the powers of $k_\alpha^2 = k^2$,

$$k \cot \delta = -\frac{1}{a} + \frac{r_0}{2} k^2 + O(k^4) \quad (7)$$

is obtained, where a is the scattering length determined from the asymptotic form of zero-energy state $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$:

$$u_0(\mathbf{r}_1, \mathbf{r}_2) = \phi(r_1) (1 - r_2/a) \pm \phi(r_2) (1 - r_1/a), \quad (8)$$

and r_0 is the effective range given by

$$r_0 = (1/4\pi) \int_0^\infty (u_0^2 - \psi_0^2) d\mathbf{r}_1 d\mathbf{r}_2 \mp 8(1 - 2/a)^2. \quad (9)$$

The cross-section is expressed as

$$\sigma = \frac{4\pi a^2}{1 + a(a - r_0)k^2 + (ar_0/2)^2 k^4}. \quad (10)$$

For the singlet state, the cross-section can also be expressed by using the function of the negative ion state $\psi_g(\mathbf{r}_1, \mathbf{r}_2)$. For that, (6) is extended to the negative energy state by putting $k_\beta = -i\gamma$, $\cot \delta_\beta = -i$. The result is

$$k \cot \delta = -\gamma + (\rho/2)(\gamma^2 + k^2) + O((\gamma^2 + k^2)^2), \quad (11)$$

where

$$\rho = \frac{1}{\gamma} - \frac{1}{4\pi} \int_0^\infty \psi_g^2 d\mathbf{r}_1 d\mathbf{r}_2, \quad (12)$$

$$\psi_g(\mathbf{r}_1, \mathbf{r}_2) \rightarrow u_g(\mathbf{r}_1, \mathbf{r}_2) \equiv \phi(r_1) \frac{\exp(-\gamma r_2)}{r_2} + \phi(r_2) \frac{\exp(-\gamma r_1)}{r_1}, \quad (13)$$

and the cross-section is given by

$$\sigma_+ = \frac{4\pi}{(\gamma^2 + k^2) [1 - \gamma(\rho + \rho^2(\gamma^2 + k^2)/4)]}. \quad (14)$$

If $\rho = r_0$ ("shape-independent" assumption) is assumed, the following relation holds:

$$\gamma = \frac{1}{a_s} + \frac{r_{0s}}{2} \gamma^2. \quad (15)$$

The numerical values of a , r_0 estimated from the existing data of calculations by various authors will be tabulated below.

A) Massey-Moiseiwitsch. They included the exchange and performed two kinds of variational calculations, the one neglecting, and the other including the polarization. The data for $k=0$ being not given, a and r_0 are estimated from those of $k=0.1, 0.2$, and 0.3 .

B) Borowitz-Greenberg. They used 3-parameter trial functions for the zero energy state. The asterisk indicates the values deduced from (15) for a_s obtained by the variational method and $\gamma=0.236$ estimated by Branscomb, and $\dagger$ those calculated from energy dependent approximate functions.

C) Seaton. He tried various methods in solving the zero energy state. The values, polarization neglected, are deduced from the accurate numerical integration including the exchange, and, polarization included, from the 3-parameter trial function.

D) We solved the zero energy equation by a method described in the next section. r_0 is calculated by (9).

E) We also calculated ρ by (12), using the 20-parameter function of Hart-Herzberg,^{b)} which is normalized according to (13) with $\gamma=0.236$, and

$$\rho = 3.37 \simeq r_0$$

	a_s	r_{0s}	a_t	r_{0t}	
A	7.6	4.5	2.34	1.37	polarization neglected
	7.08	2.34	2.34	1.12	polarization included
B	8.16	4.04*	2.352	0.808†	polarization neglected
	7.74	3.11†			polarization included
C	8.058		2.347		polarization neglected
	7.01		2.33		polarization included
D	9.02		2.350	1.29	first approximation
	7.88		2.346		second approximation
E	7.03	3.37			

is found. This value of ρ may be fairly accurate, in view of the reliability of the H^- function. Then (15) gives

$$a_s = 7.03.$$

We shall mention the applicability of the effective range theory to the electron-hydrogen scattering. To ensure the validity of the approximation assumed here, the contribution from the third term of (7) (or (11)) must be estimated. However, we feel that this approximation seems to be valid when the incident energy (and also the binding energy) of the electron is smaller than the kinetic energy of the electron inside the Bohr radius. If this is the case, the result: $a_s = 7.03$ will be very accurate, with an error possibly within a few percents.

§ 3. Variation-perturbation method

As has been remarked in the introduction, our problem of three bodies with two electrons and an infinitely heavy nucleus is the simplest of the many-body problems in quantum mechanics. But we have not on hand even a full knowledge of the analytical property of the state function at the singularities. The most effective approach practicable at the present stage would be the variational method. Indeed, for the H^- ion, very accurate calculations⁵⁾ have been performed with a large number of parameters. On the other hand, in the scattering problem, only three parameters have been employed, among which only one is responsible for the polarization. It would be worth while to look into the effect of polarization in a more systematic way.

The second Born approximation is certainly one of the powerful methods to see the general tendency of this effect.⁶⁾ However, for the low energy electron, this is not a convenient method to give a good approximation. Here an attempt is given to solve the problem by a mixed use of the Born approximation and the variational method, which is also equivalent to finding F_n approximately, when the exact solution is expressed in a form⁷⁾

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\sum_n + \int \right) \{ \phi_n(\mathbf{r}_2) F_n(\mathbf{r}_1) \pm \phi_n(\mathbf{r}_1) F_n(\mathbf{r}_2) \}.$$

The general idea has already been put forward in a paper⁸⁾ by one of the authors (T. O.). Here the procedure is described briefly, with a special attention to the degree of approximation.

Now the problem is to solve the equation

$$H\psi_k(\mathbf{r}_1, \mathbf{r}_2) = E_k\psi_k(\mathbf{r}_1, \mathbf{r}_2),$$

$$E_k = -\frac{1}{2} + \frac{k^2}{2}, \quad H = -\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}, \quad (16)$$

where ψ_k is normalized as $(\psi_k, \psi_{k'}) = \delta(k - k')$, the inner product (φ, ψ) being defined as $\iint \varphi(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$. Let an approximate solution in the Hartree-Fock approximation be

$$\varphi_{00}(\mathbf{r}_1, \mathbf{r}_2) = \phi_0(\mathbf{r}_1)f(\mathbf{r}_2) \pm \phi_0(\mathbf{r}_2)f(\mathbf{r}_1), \quad \phi_0(r) = e^{-r}/\sqrt{\pi}, \quad (17)$$

where $f(r)$ is taken, with two adjustable parameters a and b , as

$$f(r) = (1/r) \{ (1 - e^{-r}) (1 + be^{-r}) - r/a \} \quad (18)$$

Let the other approximate functions to constitute a complete system corresponding to excited states of the hydrogen atom ϕ_n be

$$\varphi_{n,k} = \frac{1}{2\pi} \left\{ \phi_n(r_1) \frac{\sin kr_2}{r_2} \pm \phi_n(r_2) \frac{\sin kr_1}{r_1} \right\}, \quad (19)$$

to which the ion state φ_g will also be included. Then we find

$$\begin{aligned} \psi_{0,0} = \varphi_{0,0} - \sum_{n=0}^{\infty} \int_0^{\infty} \frac{(\varphi_{n,k}(H + \frac{1}{2})\varphi_{0,0})}{E_{n,k} - E_{0,0}} \varphi_{n,k} dk \\ + (2/\gamma^2) (\varphi_g, (H + 1/2)\varphi_{0,0}) \varphi_g + O(\partial\psi_{0,0}, \partial\psi_{i,k}), \end{aligned} \quad (20)$$

where $E_{0,0} = -1/2$, $E_{n,k} = k^2/2 - 1/2(n+1)^2$. The order of the errors is estimated as follows. Let the error of $\varphi_{i,k}$ be $\partial\psi_{i,k} \sim \mathcal{A}$, which cannot be very small for the low energy collision, and $\partial\psi_g$ is expected to be less than $\mathcal{A}$. $\varphi_{0,0}$, with two adjustable parameters, may have smaller error ε compared with $\mathcal{A}$. Thus, taking

$$\begin{aligned} \Psi_{0,0} = \varphi_{0,0} + \sum_n \int_0^{\infty} \frac{(\varphi_{n,k}(H - E_{0,0})\varphi_{0,0})}{E_{0,0} - E_{n,k}} \varphi_{n,k} dk, \\ \Psi_{0,0} = \psi_{0,0} + O(\varepsilon \cdot \mathcal{A}) \end{aligned} \quad (21)$$

as the trial function to be put into the variational expression, the scattering length a is then calculated from

$$-1/a = -1/a_1 + (1/4\pi) (\varphi_2, (H - E_{0,0})\varphi_1) + O(\mathcal{A}\varphi_2 \cdot \mathcal{A}\varphi_1) \quad (22)$$

where a_1 is the scattering length determined by the asymptotic behavior of the trial function φ_1 . The approximate value of a is determined by taking $\varphi_1 = \varphi_2 = \varphi_{0,0}$ (first approx.), $\varphi_1 = \Psi_{0,0}$, $\varphi_2 = \varphi_{0,0}$ (second approx.), $\varphi_1 = \varphi_2 = \Psi_{0,0}$ (third approx.), for which $1/a$ will contain the errors ε^2 , $\varepsilon^2\mathcal{A}$, $\varepsilon^2\mathcal{A}^2$ respectively. (In the Born approximation the unperturbed functions are used for both φ_1 and φ_2). The second approximation in the Table is calculated retaining only $n=0$ (ground state) and 1 ($2s$ of hydrogen atom) in the summation. The parameters in (18) are determined by the Hulthén variational method as $a_s = 9.02$, $b_s = -0.396$, $a_t = 2.350$, $b_t = 0.312$.

§ 4. Summary

a) Singlet state. The effective range theory is developed for e-H scattering. According to the theory, the effective range has been calculated by making use of the H^- ion wave function, which was obtained by Hart and Herzberg very accurately, by the variational method. The effective range is found to be $r_{0s} = 3.37$. Using the binding

energy (affinity) of H^- 0.0278 which was obtained by Midtdal and Hylleraas with the variational method, the scattering length is found to be $a_s=7.03$. The values of a_s , r_{0s} obtained are estimated to be very accurate, the errors will be of the order of a few percents, because of the reliability of the H^- -function and also because the binding energy (affinity) of H^- is very small (~ 0.028) compared with the kinetic energy (~ 1) of the electron inside the Bohr radius (namely, the validity of the effective range theory in the very low energy region). It is to be noted that this agrees well with Seaton's value $a_s=7.01$, (which has an error of within 10% according to the author's estimate). On the other hand, the value $a_s=7.88$ determined from the zero energy function cannot be much relied upon, since the effect from higher excited states may not be negligible.

b) Triplet state. In this state, the effect of polarization is automatically taken into account to some extent by the anti-symmetrization of the state function, so that the first approximation $a_t=2.350$, $r_{0t}=1.29$ may not be a bad value. The accurate value of a_t in this approximation, according to Seaton, is 2.347. By including the $2s$ state only as the excited state, $a_t=2.346$ is obtained, whereas Seaton obtained $a_t=2.33$ in his calculation including the polarization.

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An Attempt at Reformulating Pion-Nucleon Interaction, II

—Scattering of Antiproton by Nucleon—

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Scattering of antiproton by nucleon is calculated assuming "nucleonic charge independence", in which nucleon and antinucleon are assumed to correspond to the third component of an angular momentum in the charge space and its conservation is assumed. It is shown that according to this assumption, the elastic and the charge exchange parts of the antinucleon-nucleon scattering are related to the nucleon-nucleon scattering in a simple way, just as neutron-proton scattering is related to the proton-proton scattering by charge independence. Explicit results are given for the total cross sections and the angular distributions of the elastic and the charge exchange parts of ($\bar{p}p$) scattering and for the elastic part of ($\bar{p}n$) scattering. As far as the comparison with experiment is possible, the result predicted by the theory is not unreasonable.

§ 1. Introduction

In a previous paper,¹⁾ we proposed a scheme in which nucleon and antinucleon were assumed to correspond to the third component of an angular momentum in the charge space. It was shown that if pion-nucleon interaction was assumed as invariant under rotations in I and K -spaces, it could not be local, especially the part responsible for the creation and the annihilation of nucleon pairs. It was conjectured that this non-locality might be responsible for the large annihilation cross section.

In addition to this, it is expected that, if the conservation of K —which we shall call nucleonic charge independence hereafter—is assumed, the antinucleon-nucleon scattering might be related to the nucleon-nucleon scattering in a simple way just as neutron-proton scattering is related to the proton-proton scattering by the charge independence. Therefore, it is expected that by examining this relation, we could check the validity of the assumption of nucleonic charge independence, or conversely, we could find a new method of approach to the problem of antinucleon-nucleon scattering. The purpose of this paper is to discuss these points in some details.

§ 2. Scattering of antiproton by nucleon

According to I , proton, neutron, antiproton and antineutron are specified by I_3 and K_3 as follows:

	I_3	K_3	
p	$1/2$	$1/2$	(2.1)
$\bar{p}$	$-1/2$	$-1/2$	
n	$-1/2$	$1/2$	
$\bar{n}$	$1/2$	$-1/2$	

Therefore, for a system composed of a nucleon and an antinucleon, there can exist four states corresponding to the triplet and singlet states of I and K . In the following we shall calculate the scattering of such system assuming the conservation of I and K .*

1) ($\bar{p}p$) scattering

Let us introduce the following notations :

I_{11}, I_{10}, I_{1-1}	: triplet eigenfunction for I
I_0	: singlet eigenfunction for I
K_{11}, K_{10}, K_{1-1}	: triplet eigenfunction for K
K_0	: singlet eigenfunction for K .

In terms of these eigenfunctions, free ($\bar{p}p$) system can be written as

$$(1/2) (I_{10} - I_0) (K_{10} - K_0) e^{ikz} \chi(s, m_s), \quad (2.2)$$

where $\chi(s, m_s)$ is the usual spin eigenfunction. (2.2) must be antisymmetrized according to the Pauli principle. After antisymmetrization we get

$$(1/\sqrt{2}) (I_{10}K_{10} + I_0K_0) \psi_A - (1/\sqrt{2}) (I_0K_{10} + I_{10}K_0) \psi_S, \quad (2.3)$$

where ψ_A and ψ_S are antisymmetric and symmetric parts of the spatial part of (2.2), and are explicitly given by**

$$\begin{aligned} \psi_A = & \frac{i\lambda\sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-S|}^{J+S} \frac{1 + (-1)^{l+s}}{2} i^l \sqrt{2l+1} \\ & \times C_{ls}(JM; 0 m_s) \{e^{-i(kr-l\pi/2)} - e^{i(kr-l\pi/2)}\} \mathcal{Y}_{Jl}^M, \end{aligned} \quad (2.4)$$

and

$$\begin{aligned} \psi_S = & \frac{i\lambda\sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-S|}^{J+S} \frac{1 - (-1)^{l+s}}{2} i^l \sqrt{2l+1} \\ & \times C_{ls}(JM; 0 m_s) \{e^{-i(kr-l\pi/2)} - e^{i(kr-l\pi/2)}\} \mathcal{Y}_{Jl}^M, \end{aligned}$$

where $\mathcal{Y}_{Jl}^M$ is the spin angle wave function

$$\mathcal{Y}_{Jl}^M = \sum_{m_l=-l}^l \sum_{m_s=-s}^s C_{ls}(JM; m_l m_s) Y_{lm_l}(\theta\varphi) \chi(s, m_s), \quad (2.5)$$

* Calculations in this section are made along the scheme given by Blatt and Biedenharn². As for the details of the calculation not described here, reader should refer to their paper.

** We assumed that the interaction hamiltonian is symmetric with respect to σ_p and $\sigma_{\bar{p}}$. Therefore $(\sigma_p + \sigma_{\bar{p}})^2$ is a constant of motion, and the triplet and the singlet scattering can be treated separately.

and $C_{ls}(JM; m_l m_s)$ is the Clebsch-Gordan coefficient.

In the presence of the interaction, outgoing parts of (2.3) are transformed by the S -matrix. Since we have assumed that I and K were conserved, S -matrix is diagonal in I and K . We write the matrix element corresponding to the transition from l to l' in the state with the total angular momentum J as

$$S^J(IKll'; s),$$

and the outgoing wave as

$$\begin{aligned} & \frac{i\hat{k}\sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{\ell=|J-s|}^{J+s} \sum_{\ell'=|J-s|}^{J+s} C_{ls}(JM; 0 m_s) i^{\ell'} \sqrt{2\ell+1} e^{i(kr-l\pi/2)} \mathcal{O}_{Jls}^J M \\ & \times \frac{1}{\sqrt{2}} \left[\frac{1+(-1)^{\ell+s}}{2} \{S^J(11'l'; s) I_{10}K_{10} + S^J(00'l'; s) I_0K_0\} \right. \\ & \left. - \frac{1-(-1)^{\ell+s}}{2} \{S^J(01'l'; s) I_0K_{10} + S^J(10'l'; s) I_{10}K_0\} \right]. \end{aligned} \quad (2.6)$$

Here terms in $\{ \}$ can be written as

$$\begin{aligned} & S^J(11'l'; s) I_{10}K_{10} + S^J(00'l'; s) I_0K_0 \\ & = (1/2) \{S^J(11'l'; s) + S^J(00'l'; s)\} (I_{10}K_{10} + I_0K_0) \\ & \quad + (1/2) \{S^J(11'l'; s) - S^J(00'l'; s)\} (I_{10}K_{10} - I_0K_0), \end{aligned}$$

and

$$\begin{aligned} & S^J(01'l'; s) I_0K_{10} + S^J(10'l'; s) I_{10}K_0 \\ & = (1/2) \{S^J(01'l'; s) + S^J(10'l'; s)\} (I_0K_{10} + I_{10}K_0) \\ & \quad + (1/2) \{S^J(01'l'; s) - S^J(10'l'; s)\} (I_0K_{10} - I_{10}K_0). \end{aligned} \quad (2.7)$$

Here

$$\begin{aligned} I_{10}K_{10} + I_0K_0 &= (p \bar{p}) + (\bar{p} p), \\ I_{10}K_{10} - I_0K_0 &= (n \bar{n}) + (\bar{n} n), \\ I_0K_{10} + I_{10}K_0 &= (p \bar{p}) - (\bar{p} p), \end{aligned} \quad (2.8)$$

and

$$I_0K_{10} - I_{10}K_0 = -(n \bar{n}) + (\bar{n} n),$$

where $(\bar{p} p)$ $((\bar{n} n))$ and $(p p)$ $((n \bar{n}))$ respectively denote the states where the first particle is antiproton (antineutron) and the second particle is proton (neutron), and the first particle is proton (neutron) and the second particle is antiproton (antineutron). Therefore, the first and the second terms of each expressions of (2.7) respectively correspond to the elastic $(\bar{p} + p \rightarrow \bar{p} + p)$ and the charge exchange $(\bar{p} + p \rightarrow \bar{n} + n)$ scattering.

In the following we shall discuss the elastic scattering at first. The scattered wave for elastic scattering is obtained by taking the difference between the parts correspond-

ing to the outgoing waves of antiproton in (2.6) and those in (2.3). Here it should be noticed that in terms containing $(\bar{p} \bar{p})$, the role of the first and the second particle must be exchanged. Thus, ϕ_A changes the sign, and we get

$$\begin{aligned} \phi_{el} = & \frac{i\lambda\sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-s|}^{J+s} \sum_{l'=|J-s|}^{J+s} C_{ls}(JM; 0m_s) i^l \sqrt{2l+1} e^{i(kr-l\pi/2)} \mathcal{Y}_{Jls}^M \\ & \times \frac{1}{\sqrt{2}} \left[\frac{1+(-1)^{l+s}}{2} \left\{ \delta_{ll'} - \frac{1}{2} [S^J(11 l' l; s) + S^J(00 l' l; s)] \right\} \right. \\ & \left. + \frac{1-(-1)^{l+s}}{2} \left\{ \delta_{ll'} - \frac{1}{2} [S^J(01 l' l; s) + S^J(10 l' l; s)] \right\} \right] [(\bar{p} p) - (p \bar{p})]. \end{aligned} \quad (2.9)$$

Decomposing $\mathcal{Y}_{Jls}^M$ we can write this as

$$\phi_{el} = i\lambda \frac{e^{ikr}}{r} \sum_{m'_s=-s}^s q_{m'_s; m_s}(\theta, \varphi) \chi(s, m'_s), \quad (2.10)$$

with

$$\begin{aligned} q_{m'_s; m_s}(\theta, \varphi) = & \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-s|}^{J+s} \sum_{l'=|J-s|}^{J+s} \sum_{\mu'=-l'}^{l'} i^{l-l'} \sqrt{\pi(2l+1)} C_{ls}(JM; 0m_s) C_{l's}(JM; \mu'm'_s) \\ & \times \frac{1}{\sqrt{2}} \left[\frac{1+(-1)^{l+s}}{2} \{ \delta_{ll'} - (1/2) [S^J(11 l' l; s) + S^J(00 l' l; s)] \} \right. \\ & \left. + \frac{1-(-1)^{l+s}}{2} \{ \delta_{ll'} - (1/2) [S^J(01 l' l; s) + S^J(10 l' l; s)] \} \right] [(\bar{p} p) - (p \bar{p})] Y_{Jls}^M(\theta, \varphi). \end{aligned} \quad (2.11)$$

Thus, the cross section from the initial state with magnetic quantum number m_s to the final state with magnetic quantum number m'_s is given by

$$d\sigma_{\bar{p}p}^{el}(m'_s; m_s) = \lambda^2 |q_{m'_s; m_s}(\theta, \varphi)|^2 d\Omega. \quad (2.12)$$

Total cross section for unpolarized beam can be obtained from (2.12) by summing over m'_s and averaging over m_s . Explicitly, it is given by

$$\begin{aligned} d\sigma_{\bar{p}p}^{el}(s) = & \frac{\lambda^2}{2s+1} \sum_{m_s=-s}^s \sum_{m'_s=-s}^s d\sigma_{\bar{p}p}^{el}(m'_s; m_s) \\ = & \frac{\lambda^2}{2s+1} \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} \sum_{l'_1} \sum_{l'_2} i^{-l_1+l'_1+l_2-l'_2} K(J_1 l_1 l'_1; J_2 l_2 l'_2; s\theta) d\Omega \\ & \times \left[\frac{1+(-1)^{l_1+s}}{2} \cdot \frac{1+(-1)^{l_2+s}}{2} \{ \delta_{l'_1 l_1} - (1/2) [S^{J_1}(11 l'_1 l_1; s) + S^{J_1}(00 l'_1 l_1; s)] \}^* \right. \\ & \quad \times \{ \delta_{l'_2 l_2} - (1/2) [S^{J_2}(11 l'_2 l_2; s) + S^{J_2}(00 l'_2 l_2; s)] \} \\ & \left. + \frac{1-(-1)^{l_1+s}}{2} \cdot \frac{1-(-1)^{l_2+s}}{2} \{ \delta_{l'_1 l_1} - (1/2) [S^{J_1}(01 l'_1 l_1; s) + S^{J_1}(10 l'_1 l_1; s)] \}^* \right. \\ & \quad \times \{ \delta_{l'_2 l_2} - (1/2) [S^{J_2}(01 l'_2 l_2; s) + S^{J_2}(10 l'_2 l_2; s)] \} \end{aligned} \quad (2.13)$$

$$\begin{aligned}
 & + \frac{1 + (-1)^{l_1+s}}{2} \cdot \frac{1 - (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(11l_1'l_1; s) + S^{J_1}(00l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(01l_2'l_2; s) + S^{J_2}(10l_2'l_2; s)] \} \\
 & + \frac{1 - (-1)^{l_1+s}}{2} \cdot \frac{1 + (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(01l_1'l_1; s) + S^{J_1}(10l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(01l_2'l_2; s) + S^{J_2}(10l_2'l_2; s)] \} \Big],
 \end{aligned}$$

where

$$\begin{aligned}
 K(J_1 l_1 l_1'; J_2 l_2 l_2'; s\theta) = & \sqrt{2l_1+1} \sqrt{2l_2+1} \pi \sum_{m_s} \sum_{m_s'} \sum_{M_1} \sum_{M_2} \sum_{\mu_1'} \sum_{\mu_2'} \\
 & \times C_{l_1 s}(J_1 M_1; 0 m_s) C_{l_2 s}(J_2 M_2; 0 m_s) C_{l_1' s}(J_1 M_1; \mu_1' m_s') C_{l_2' s}(J_2 M_2; \mu_2' m_s') \quad (2.14) \\
 & \times Y_{l_1' \mu_1'}^*(\theta\varphi) Y_{l_2' \mu_2'}(\theta\varphi).
 \end{aligned}$$

Here summation over magnetic quantum numbers can be made using Racah's technique, and we get

$$d\sigma_{\bar{p}p}^{el}(s) = \frac{\lambda^2}{2s+1} \sum_{L=0}^{\infty} B_{\bar{p}p}^{el}(L, s) P_L(\cos \theta) d\Omega, \quad (2.15)$$

where

$$\begin{aligned}
 B_{\bar{p}p}^{el}(L, s) = & (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} \sum_{l_1'} \sum_{l_2'} Z(l_1 J_1 l_2 J_2; sL) Z(l_1' J_1' l_2' J_2'; sL) \\
 & \times \text{Re} \Big[\frac{1 + (-1)^{l_1+s}}{2} \cdot \frac{1 + (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(11l_1'l_1; s) + S^{J_1}(00l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(11l_2'l_2; s) + S^{J_2}(00l_2'l_2; s)] \} \\
 & + \frac{1 - (-1)^{l_1+s}}{2} \cdot \frac{1 - (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(01l_1'l_1; s) + S^{J_1}(10l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(01l_2'l_2; s) + S^{J_2}(10l_2'l_2; s)] \} \quad (2.16) \\
 & + \frac{1 + (-1)^{l_1+s}}{2} \cdot \frac{1 - (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(11l_1'l_1; s) + S^{J_1}(00l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(01l_2'l_2; s) + S^{J_2}(10l_2'l_2; s)] \} \\
 & + \frac{1 - (-1)^{l_1+s}}{2} \cdot \frac{1 + (-1)^{l_2+s}}{2} \{ \delta_{l_1'l_1} - (1/2) [S^{J_1}(01l_1'l_1; s) + S^{J_1}(10l_1'l_1; s)] \}^* \\
 & \quad \times \{ \delta_{l_2'l_2} - (1/2) [S^{J_2}(11l_2'l_2; s) + S^{J_2}(00l_2'l_2; s)] \} \Big],
 \end{aligned}$$

and $Z(l_1 J_1 l_2 J_2; sL)$ is given by

$$\begin{aligned}
 Z(l_1 J_1 l_2 J_2; sL) = & i^{L-l_1+l_2} \sqrt{(2l_1+1)(2l_2+1)(2J_1+1)(2J_2+1)} \\
 & \times W(l_1 J_1 l_2 J_2; sL) C_{l_1 l_2}(L0; 00). \quad (2.17)
 \end{aligned}$$

$W(l_1 J_1 l_2 J_2; sL)$ is the Racah coefficient.

In the following we shall neglect coupling between states with $l=J+1$ in triplet states. Then, $S^J(IK'l; s)$ can be written as

$$S^J(IK'l; s) = \delta_{l,l'} S^J(IKl; s),$$

and introducing phase shift by

$$S^J(IKl; s) = \begin{cases} \exp(2i\delta_{J,l}^s) & \text{for } K=1 \\ \eta_{J,l}^s \exp(2i\tilde{\epsilon}_{J,l}^s) & \text{for } K=0, \end{cases} \quad (2.18)$$

we can write $B_{pp}^{el}(L; s)$ as

$$\begin{aligned} B_{pp}^{el}(L, s) = (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} (Z(l_1 J_1 l_2 J_2; sL))^2 \\ \times \{ \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s) + \sin \tilde{\epsilon}_{J_1 l_1}^s \sin \tilde{\epsilon}_{J_2 l_2}^s \cos(\tilde{\epsilon}_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) \\ + \sin \delta_{J_1 l_1}^s \sin \tilde{\epsilon}_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) + \sin \tilde{\epsilon}_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_2 l_2}^s - \tilde{\epsilon}_{J_1 l_1}^s) \\ + (1/2)(1 - \eta_{J_1 l_1}^s) \cos 2\tilde{\epsilon}_{J_1 l_1}^s + (1/2)(1 - \eta_{J_2 l_2}^s) \cos 2\tilde{\epsilon}_{J_2 l_2}^s \\ + (1/4)(\eta_{J_1 l_1}^s \eta_{J_2 l_2}^s - 1) \cos 2(\tilde{\epsilon}_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) + (1/4)(\eta_{J_1 l_1}^s - 1) \cos 2(\delta_{J_2 l_2}^s - \tilde{\epsilon}_{J_1 l_1}^s) \\ + (1/4)(\eta_{J_2 l_2}^s - 1) \cos 2(\delta_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) \}. \end{aligned} \quad (2.19)$$

In (2.19) we omitted suffixes for isotopic spin. They should be taken so that they satisfy the Pauli principle.

As will be seen from (2.17), $Z(l_1 J_1 l_2 J_2; sL)$ is purely of a kinematical nature, and the dynamical features of the system are all contained in $\text{Re} \dots$ in $B_{pp}(L, s)$. We shall hereafter call the former the kinematical factor, and the latter the dynamical factor.

The total cross section is given at once from (2.15) using the relation:

$$Z(l_1 J_1 l_2 J_2; s0) = \delta_{l_1 l_2} \delta_{J_1 J_2} (-1)^{J_1 - s} \sqrt{2J_1 + 1}.$$

Thus

$$\begin{aligned} \sigma_{pp}^{el}(s) = (\pi \lambda^2 / 2s + 1) \sum_J \sum_{l_1} \sum_{l_2} (2J + 1) \\ \times \left[\frac{1 + (-1)^{l_1 + s}}{2} |\delta_{ll} - (1/2)[S^J(11l'l; s) + S^J(00l'l; s)]|^2 \right. \\ \left. + \frac{1 - (-1)^{l_1 + s}}{2} |\delta_{ll} - (1/2)[S^J(01l'l; s) + S^J(10l'l; s)]|^2 \right], \end{aligned} \quad (2.20)$$

which, neglecting coupling in triplet states, is simplified to

$$\begin{aligned} \sigma_{pp}^{el}(s) = (\pi \lambda^2 / 2s + 1) \sum_J \sum_{l_1} \sum_{l_2} (2J + 1) \{ 2 \sin^2 \delta_{Jl}^s + 2 \eta_{Jl}^s \sin^2 \tilde{\epsilon}_{Jl}^s \\ - \eta_{Jl}^s \sin^2 (\delta_{Jl}^s - \tilde{\epsilon}_{Jl}^s) + (1/4)(1 - \eta_{Jl}^s)^2 \}. \end{aligned} \quad (2.21)$$

Total cross section is given by summing (2.21) over s corresponding to singlet and triplet scattering:

$$\begin{aligned}
 \sigma_{\bar{p}p}^{el} &= (1/4) \sigma_{\bar{p}p}^{el}(0) + (3/4) \sigma_{\bar{p}p}^{el}(1) \\
 &= (\pi \lambda^2/4) \sum_J \sum_l \sum_s (2J+1) \{ 2 \sin^2 \delta_{Jl}^s + 2 \gamma_{Jl}^s \sin^2 \xi_{Jl}^s \\
 &\quad - \gamma_{Jl}^s \sin^2 (\delta_{Jl}^s - \xi_{Jl}^s) + (1/4) (1 - \gamma_{Jl}^s)^2 \}.
 \end{aligned} \tag{2.22}$$

Analogous to (2.9), the scattered wave for charge exchange scattering is given by

$$\begin{aligned}
 \psi_{ev} &= \frac{i\lambda \sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-s|}^{J+s} \sum_{l'=|J-s|}^{J+s} C_{ls}(JM; 0m_s) i^l \sqrt{2l+1} e^{i(kr-l\pi/2)} \mathcal{Y}_{Jls}^M \\
 &\quad \times \frac{1}{\sqrt{2}} \left[\frac{1+(-1)^{l+s}}{2} (-1/2) [S^J(11l'l; s) - S^J(00l'l; s)] \right. \\
 &\quad \left. - \frac{1-(-1)^{l+s}}{2} (-1/2) [S^J(01l'l; s) - S^J(10l'l; s)] \right] [(\bar{m}) - (m)].
 \end{aligned}$$

Therefore, it would be clear that the differential and the total cross section for charge exchange scattering are obtained by making following substitutions in the dynamical factors of (2.16):

$$\begin{aligned}
 \delta_{ll'} &\rightarrow (1/2) [S^J(11l'l; s) + S^J(00l'l; s)] \rightarrow (-1/2) [S^J(11l'l; s) - S^J(00l'l; s)], \\
 \delta_{l'l'} &\rightarrow (1/2) [S^J(01l'l; s) + S^J(10l'l; s)] \rightarrow (1/2) [S^J(01l'l; s) - S^J(10l'l; s)].
 \end{aligned} \tag{2.23}$$

Thus,

$$d\sigma_{\bar{p}p}^{ex}(s) = (\lambda^2/2s+1) \sum_L B_{\bar{p}p}^{ex}(L, s) P_L(\cos \theta) d\Omega, \tag{2.24}$$

with

$$\begin{aligned}
 B_{\bar{p}p}^{ex}(s) &= (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} \sum_{l_1'} \sum_{l_2'} Z(l_1 J_1 l_2 J_2; s L) Z(l_1' J_1' l_2' J_2'; s L) \\
 &\times \frac{1}{4} \text{Re} \left\{ \frac{1+(-1)^{l_1+s}}{2} \cdot \frac{1+(-1)^{l_2+s}}{2} [S^{J_1}(11l_1'l_1; s) - S^{J_1}(00l_1'l_1; s)]^* \right. \\
 &\quad \times [S^{J_2}(11l_2'l_2; s) - S^{J_2}(00l_2'l_2; s)] \\
 &\quad + \frac{1-(-1)^{l_1+s}}{2} \cdot \frac{1-(-1)^{l_2+s}}{2} [S^{J_1}(01l_1'l_1; s) - S^{J_1}(10l_1'l_1; s)]^* \\
 &\quad \times [S^{J_2}(01l_2'l_2; s) - S^{J_2}(10l_2'l_2; s)] \\
 &\quad - \frac{1+(-1)^{l_1+s}}{2} \cdot \frac{1-(-1)^{l_2+s}}{2} [S^{J_1}(11l_1'l_1; s) - S^{J_1}(00l_1'l_1; s)]^* \\
 &\quad \times [S^{J_2}(01l_2'l_2; s) - S^{J_2}(10l_2'l_2; s)] \\
 &\quad - \frac{1-(-1)^{l_1+s}}{2} \cdot \frac{1+(-1)^{l_2+s}}{2} [S^{J_1}(01l_1'l_1; s) - S^{J_1}(10l_1'l_1; s)]^* \\
 &\quad \times [S^{J_2}(11l_2'l_2; s) - S^{J_2}(00l_2'l_2; s)] \Big\},
 \end{aligned}$$

and

$$\begin{aligned} \sigma_{\bar{p}p}^{er}(s) = & (\pi\lambda^2/2s+1) \sum_J \sum_l \sum_{l'} (2J+1) \\ & \times \left[\frac{1+(-1)^{l+s}}{2} |S^J(11l'l; s) - S^J(00l'l; s)|^2 + \right. \\ & \left. + \frac{1-(-1)^{l+s}}{2} |S^J(01l'l; s) - S^J(10l'l; s)|^2 \right]. \quad (2.25) \end{aligned}$$

Therefore, under the same approximation as before, we get

$$\begin{aligned} B_{\bar{p}p}^{er}(L, s) = & (1/16) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} (Z(l_1 J_1 l_2 J_2; s, L))^2 (-1)^{l_1+l_2} \\ & \times \{ \cos 2(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s) - \eta_{J_3 l_1}^s \cos 2(\tilde{\epsilon}_{J_1 l_1}^s - \delta_{J_2 l_2}^s) \\ & - \eta_{J_2 l_2}^s \cos 2(\tilde{\epsilon}_{J_2 l_2}^s - \delta_{J_3 l_1}^s) + \eta_{J_3 l_1}^s \eta_{J_2 l_2}^s \cos 2(\tilde{\epsilon}_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) \}, \quad (2.26) \end{aligned}$$

and

$$\sigma_{\bar{p}p}^{er} = (\pi\lambda^2/4) \sum_J \sum_l \sum_s (2J+1) \{ \eta_{Jl}^s \sin^2(\delta_{Jl}^s - \tilde{\epsilon}_{Jl}^s) + (1/4)(1 - \eta_{Jl}^s)^2 \}. \quad (2.27)$$

Annihilation cross section is obtained by calculating the decrease of the outgoing flux relative to that for the free system. Since annihilation occurs only in channel corresponding to $K=0$, we have

$$\begin{aligned} \sigma_{\bar{p}p}^{an}(s) = & (\pi\lambda^2/2s+1) (1/2) \sum_J \sum_l \sum_{l'} (2J+1) \\ & \times \left\{ \frac{1+(-1)^{l+s}}{2} (\delta_{ll'} - |S^J(00l'l; s)|^2) + \frac{1-(-1)^{l+s}}{2} (\delta_{ll'} - |S^J(10l'l; s)|^2) \right\}, \quad (2.28) \end{aligned}$$

from which we have

$$\sigma_{\bar{p}p}^{an} = (\pi\lambda^2/8) \sum_J \sum_l \sum_s (2J+1) \{ 1 - (\eta_{Jl}^s)^2 \} \quad (2.29)$$

neglecting couplings in the triplet states.

2) ($\bar{p}n$) scattering

Wave function for free ($\bar{p}n$) system satisfying the Pauli principle is given by

$$I_{1-1} K_{10} \psi_A - I_{1-1} K_0 \psi_S. \quad (2.30)$$

Thus, analogous to (2.9), the scattered wave is given by

$$\begin{aligned} & \frac{i\lambda\sqrt{\pi}}{r} \sum_{J=0}^{\infty} \sum_{M=-J}^J \sum_{l=|J-s|}^J \sum_{l'=|J-s|}^{J+s} C_{ls}(JM; 0m_s) i^l \sqrt{2l+1} e^{i(kr-l\pi/2)} \mathcal{O}_{Jl's}^M \\ & \times \frac{1}{\sqrt{2}} \left[\frac{1+(-1)^{l+s}}{2} \{ \delta_{ll'} - S^J(11l'l; s) \} + \frac{1-(-1)^{l+s}}{2} \{ \delta_{ll'} - S^J(10l'l; s) \} \right] \\ & \times [(\bar{p}n) - (n\bar{p})]. \quad (2.31) \end{aligned}$$

Therefore, calculation can be made entirely analogous to that of $(\bar{p}p)$. As for the elastic part, we get the result by making following substitutions in the dynamical factors :

$$\delta_{ll} \rightarrow (1/2)[S^J(11'l; s) + S^J(00'l; s)] \rightarrow \delta_{ll} - S^J(11'l; s),$$

and

$$\delta_{ll} \rightarrow (1/2)[S^J(01'l; s) + S^J(10'l; s)] \rightarrow \delta_{ll} - S^J(10'l; s).$$

Thus,

$$d\sigma_{\bar{p}n}^{el}(s) = (\lambda^2/2s+1) \sum_L B_{\bar{p}n}^{el}(L, s) P_L(\cos \theta) d\Omega, \quad (2.32)$$

with

$$\begin{aligned} B_{\bar{p}n}^{el}(L, s) = & (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} \sum_{l_1'} \sum_{l_2'} Z(l_1 J_1 l_2 J_2; s L) Z(l_1' J_1 l_2' J_2; s L) \\ & \times \text{Re} \left[\frac{1 + (-1)^{l_1+s}}{2} \frac{1 + (-1)^{l_2+s}}{2} \{ \delta_{l_1 l_1'} - S^{J_1}(11 l_1' l_1; s) \}^* \right. \\ & \quad \times \{ \delta_{l_2 l_2'} - S^{J_2}(11 l_2' l_2; s) \} \\ & + \frac{1 - (-1)^{l_1+s}}{2} \frac{1 - (-1)^{l_2+s}}{2} \{ \delta_{l_1 l_1'} - S^{J_1}(10 l_1' l_1; s) \}^* \\ & \quad \times \{ \delta_{l_2 l_2'} - S^{J_2}(10 l_2' l_2; s) \} \\ & + \frac{1 + (-1)^{l_1+s}}{2} \frac{1 - (-1)^{l_2+s}}{2} \{ \delta_{l_1 l_1'} - S^{J_1}(11 l_1' l_1; s) \}^* \\ & \quad \times \{ \delta_{l_2 l_2'} - S^{J_2}(10 l_2' l_2; s) \} \\ & + \frac{1 - (-1)^{l_1+s}}{2} \frac{1 + (-1)^{l_2+s}}{2} \{ \delta_{l_1 l_1'} - S^{J_1}(10 l_1' l_1; s) \}^* \\ & \quad \times \{ \delta_{l_2 l_2'} - S^{J_2}(11 l_2' l_2; s) \} \left. \right], \end{aligned} \quad (2.33)$$

which is simplified, in the same approximation as before, to

$$\begin{aligned} & (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2}' (Z(l_1 J_1 l_2 J_2; s L))^2 \\ & \times [4 \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s) + \{1 - \eta_{J_1 l_1}^s \cos 2\tilde{\epsilon}_{J_1 l_1}^s - \eta_{J_2 l_2}^s \cos 2\tilde{\epsilon}_{J_2 l_2}^s \\ & + \eta_{J_1 l_1}^s \eta_{J_2 l_2}^s \cos 2(\tilde{\epsilon}_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s)\} + \{2 - \cos 2\delta_{J_1 l_1}^s - \eta_{J_2 l_2}^s \cos 2\tilde{\epsilon}_{J_2 l_2}^s \\ & + \eta_{J_2 l_2}^s \cos 2(\delta_{J_1 l_1}^s - \tilde{\epsilon}_{J_2 l_2}^s) - \cos 2\delta_{J_2 l_2}^s - \eta_{J_1 l_1}^s \cos 2\tilde{\epsilon}_{J_1 l_1}^s + \eta_{J_1 l_1}^s \cos 2(\delta_{J_2 l_2}^s - \tilde{\epsilon}_{J_1 l_1}^s)\}]. \end{aligned} \quad (2.34)$$

In $(\bar{p}n)$ system $I=1$. Therefore, the Pauli principle restricts possible l when s and K are given. $\sum_l'$ in (2.34) means summation over those l only which are consistent with this restriction.

The total cross section is given by

$$\sigma_{\bar{p}n}^{el}(s) = (\pi \lambda^2/2s+1) \sum_J \sum_{\ell} \sum_{\ell'} (2J+1)$$

$$\times \left\{ \frac{1 - (-1)^{l+s}}{2} (\delta_{ll'} - S^J(11'l'; s))^2 + \frac{1 - (-1)^{l+s}}{2} (\delta_{ll'} - S^J(10'l'; s))^2 \right\}, \quad (2.35)$$

from which we have

$$\sigma_{\bar{p}n}^{el} = \pi \lambda^2 \sum_J \sum_{l'} \sum_s (2J+1) \{ \sin^2 \delta_{Jl'}^s + \tau_{Jl'}^s \sin^2 \hat{\epsilon}_{Jl'}^s + (1/4) (1 - \tau_{Jl'}^s)^2 \} \quad (2.36)$$

neglecting coupling in the triplet states.

The annihilation cross section is given by

$$\sigma_{\bar{p}n}^{an}(s) = (\pi \lambda^2 / 2s + 1) \sum_J \sum_{l'} \sum_{l''} (2J+1) \frac{1 - (-1)^{l+s}}{2} (\delta_{ll'} - S^J(10'l'; s))^2, \quad (2.37)$$

which gives

$$\sigma_{\bar{p}n}^{an} = (\pi \lambda^2 / 4) \sum_J \sum_{l'} \sum_s (2J+1) \{ 1 - (\tau_{Jl'}^s)^2 \} \quad (2.38)$$

in our approximation.

For the latter purpose, we shall give here formula for (pn) and (pp) scattering. They are given by making following substitutions in corresponding formulas for $(\bar{p}p)$ and $(\bar{p}n)$ scatterings.

$$\begin{aligned} (pn): \quad & \delta_{ll'} = (1/2) [S^J(11'l'; s) + S^J(00'l'; s)] \rightarrow \delta_{ll'} - S^J(11'l'; s), \\ & \delta_{ll'} = (1/2) [S^J(01'l'; s) + S^J(10'l'; s)] \rightarrow \delta_{ll'} - S^J(01'l'; s), \\ (pp): \quad & \delta_{ll'} = S^J(11'l'; s) \rightarrow \sqrt{2} [\delta_{ll'} - S^J(11'l'; s)], \\ & \delta_{ll'} = S^J(10'l'; s) \rightarrow 0. \end{aligned}$$

Thus,

$$d\sigma_{pn}(s) = (\pi \lambda^2 / 2s + 1) \sum_L B_{pn}(L, s) P_L(\cos \theta) d\Omega, \quad (2.39)$$

with

$$\begin{aligned} B_{pn}(L, s) = & \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} (Z(l_1 J_1 l_2 J_2; s, L))^2 \\ & \times \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos (\delta_{J_1 l_1} - \delta_{J_2 l_2}), \end{aligned} \quad (2.40)^*$$

and

$$\sigma_{pn} = \pi \lambda^2 \sum_J \sum_{l'} \sum_s (2J+1) \sin^2 \delta_{Jl'}^s, \quad (2.41)$$

and

$$d\sigma_{pp}(s) = (\lambda^2 / 2s + 1) \sum_L B_{pp}(L, s) P_L(\cos \theta) d\Omega, \quad (2.42)$$

with

* In (2.40) - (2.44) couplings in triplet states are of course neglected.

$$B_{pp}(L, s) = 2 \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2}' (\mathcal{Z}(l_1 J_1 l_2 J_2; s L))^2 \times \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s), \quad (2.43)$$

and

$$\sigma_{pp} = 2\pi \lambda^2 \sum_J \sum_l \sum_s (2J+1) \sin^2 \delta_{Jl}^s, \quad (2.44)$$

which agree, of course, with results given in usual literatures.

§ 3. Comparison with experiment

In this section we shall discuss the results obtained in § 2 in some details. To make the comparison with experiment concrete, it is necessary to simplify the formulas obtained in § 2. In the following we shall neglect ξ_{Jl}^s against δ_{Jl}^s from the following reason. In the state corresponding to $K=0$, the annihilation cross section is very large, and moreover to reproduce the observed value (90mb at 450 Mev), the range of the interaction must be taken considerably large, at least of the same order of magnitude with the range of nuclear force. Therefore, the intensity of the incident beam will be strongly reduced in this region, and the phase shifts will be correspondingly reduced.* We also assume that η_{Jl}^s is independent of s and l .

Writing down quantities comparable with experiments directly in this approximation, we get following results.

* If we describe the annihilation by an imaginary potential $-iW(r)$, the intensity of the incident antiproton after traversing from r_0 to r in the imaginary region is given by

$$|\psi(r)|^2 \propto \exp\left[-\int_{r_0}^r (W(r)/E_0) k_0 dr\right],$$

where E_0 is the incident energy and k_0 is given by $k_0 = \sqrt{ME_0/\hbar^2}$. Thus, if we assume for $W(r)$

$$W(r) = W_0 e^{-(r/a)/(r/a)},$$

we get

$$|\psi(r)|^2 \propto \exp[(W_0/E_0)(k_0 a) E_i(-r/a)],$$

here $E_i(-r/a)$ is

$$E_i(-r/a) = -\int_{r/a}^{\infty} e^{-t}/t \cdot dt.$$

Experimental values at 450 Mev are reproduced approximately by taking $a = (\hbar/\mu c)$ and $W_0 = 70$ Mev. Substituting these values,

$$|\psi(r)|^2 \propto \exp[0.9 E_i(-r/a)].$$

From this expression we can estimate that at about 450 Mev $|\psi(r)|^2$ is reduced by about factor 4, 2, 1.5... at r corresponding to the impact parameter for s, p, d ... waves respectively. Therefore if antinucleon-nucleon potential is not so much different from the nucleon-nucleon potential, and if it is not so strong as compared with E_0 , and the computational method such as the Born approximation can be used, we may expect that the ξ_{Jl}^s 's are smaller than δ_{Jl}^s 's by about factor 4, 2, 1.5... Unfortunately, this conclusion is sensitive to the form of $W(r)$, and if we assume shallow and long ranged form for $W(r)$ instead of singular one such as the Yukawa type such reduction cannot be expected.

1. ($\bar{p}p$) scattering

$$i) \quad \sigma_{\bar{p}p}^{el} = (1/2) \sigma_{pp} + (\pi \lambda^2/4) \sum_J (2J+1) (1-\eta_J)^2 - (\pi \lambda^2/4) \sum_{Jl_2} (2J+1) \eta_J \sin^2 \delta_{Jl_2}^s, \quad (3.1)$$

$$ii) \quad \sigma_{\bar{p}p}^{ex} = (\pi \lambda^2/4) \sum_J (2J+1) (1-\eta_J)^2 + (\pi \lambda^2/4) \sum_{Jl_2} (2J+1) \eta_J \sin^2 \delta_{Jl_2}^s, \quad (3.2)$$

$$iii) \quad \sigma_{\bar{p}p}^{an} = (\pi \lambda^2/2) \sum_J (2J+1) (1-\eta_J^2), \quad (3.3)$$

$$iv) \quad B_{\bar{p}p}^{el}(L, s) = (1/4) B_{pp}(L, s) + (1/4) \sum_{J_1 J_2 l_1 l_2} (Z(l_1 J_1 l_2 J_2; s L))^2 \\ \times \{ (1/4) (1-\eta_{J_1}) (1-\eta_{J_2}) + (1/2) (1-\eta_{J_1}) \sin^2 \delta_{J_2 l_2}^s \\ + (1/2) (1-\eta_{J_2}) \sin^2 \delta_{J_1 l_1}^s \}, \quad (3.4)$$

$$v) \quad B_{\bar{p}p}^{ex}(L, s) = (1/4) \sum_{J_1 J_2 l_1 l_2} (Z(l_1 J_1 l_2 J_2; s L))^2 (-1)^{l_1+l_2} \\ \times \{ \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s) \\ + (1/4) (1-\eta_{J_1}) (1-\eta_{J_2}) - (1/2) (1-\eta_{J_1}) \sin^2 \delta_{J_2 l_2}^s - (1/2) (1-\eta_{J_2}) \sin^2 \delta_{J_1 l_1}^s \}. \quad (3.5)$$

2. ($\bar{p}n$) scattering

$$i) \quad \sigma_{\bar{p}n}^{el} = (1/2) \sigma_{pn} + (\pi \lambda^2/4) \sum_J (2J+1) (2+(-1)^J) (1-\eta_J)^2, \quad (3.6)$$

$$ii) \quad \sigma_{\bar{p}n}^{an} = (\pi \lambda^2/4) \sum_J (2J+1) (2+(-1)^J) (1-\eta_J^2), \quad (3.7)$$

$$iii) \quad B_{\bar{p}n}^{el}(L, s) = (1/2) B_{pn}(L, s) + \sum_{J_1 J_2} \sum_{l_1 l_2}' (Z(l_1 J_1 l_2 J_2; s L))^2 \\ \times \{ (1/4) (1-\eta_{J_1}) (1-\eta_{J_2}) + (1/2) (1-\eta_{J_2}) \sin^2 \delta_{J_1 l_1}^s \\ + (1/2) (1-\eta_{J_1}) \sin^2 \delta_{J_2 l_2}^s \}. \quad (3.8)$$

One feature of these results is the appearance of a factor $1/2$ in the expression for σ^{an} , which is due to the fact that under the assumption of nucleonic charge independence, the part contributing to the annihilation is only one half of the incident flux corresponding to $K=0$. Therefore, we must take the range of annihilation larger than usually assumed to get observed values.* This means that partial waves higher than that usually assumed can contribute to the annihilation, and therefore the scattering angle of shadow scattering becomes correspondingly smaller.

Another feature is the appearance of σ_{pp} (σ_{pn}) and $B_{pp}(L, s)$ ($B_{pn}(L, s)$) in the expression for $\sigma_{\bar{p}p}^{el}$ ($\sigma_{\bar{p}n}^{el}$) and $B_{\bar{p}p}^{el}(L, s)$ ($B_{\bar{p}n}^{el}(L, s)$), which is due to the presence of

* If we assume

$$\eta_J = \begin{cases} \eta & \text{for } J \leq R/\lambda \\ 0 & \text{for } J \geq R/\lambda, \end{cases}$$

σ^{an} is given by

$$\sigma^{an} \simeq (1/2) \pi R^2 (1-\eta^2).$$

In this approximation, therefore, we must take $R \sqrt{2}$ times larger than usually assumed.

states corresponding to $K=1$. As expected before, this enables us to relate some parts of antinucleon-nucleon scattering to nucleon-nucleon scattering, and it is expected that these relations can be used to check the validity of our assumption.

Let us begin with the angular distribution of elastic ($\bar{p}p$) scattering. Although direct measurement has not yet been made, we can draw same conclusions on the angular distribution from data on the attenuation cross section measured under different conditions. Data now available is as follows :

Table I

Author	Energy	Cut off angle	Total cross section	Annihilation cross section
I) Chamberlain <i>et al</i> ³⁾	457 MeV	14°	105±8mb	87±7mb
II) „ ³⁾	457 MeV	20°	102±8mb	87±7mb
III) Piccioni <i>et al</i> ⁴⁾	500 MeV	3°	97±4mb	

The difference between the total cross section and the annihilation cross section gives the sum of elastic scattering ($\bar{p}+p \rightarrow \bar{p}+p$) outer than the cut off angle and the exchange scattering ($\bar{p}+p \rightarrow \bar{n}+n$). Therefore, the differences between I) and III), II) and III) and I) and II) give elastic scattering cross section between 3° and 14°, 3° and 20° and 14° and 20° respectively. Unfortunately, the error is very large at present. We may say as a very crude feature, however, that the forward scattering is relatively small, and the main part might be backward scattering. There is some difficulty to understand this feature from the usual theory, since if we assume that the real part of the phase shift is small by the same reason as we neglected $\hat{\epsilon}_{JI}^s$ against δ_{JI}^s , we must assume that the elastic scattering is mainly shadow scattering. If nucleonic charge independence is assumed, the scattered amplitude becomes the superposition of (pn) scattering and shadow scattering as seen from (3.4). In the former, the main part is the backward scattering. Therefore, if the shadow scattering can be made small, the main part of the elastic scattering can be backward scattering. This is made possible by assuming a large and rather transparent annihilating region.

Next we shall discuss the total cross section. From (3.1) and (3.2) we get

$$\sigma_{\bar{p}p}^{el} + \sigma_{\bar{p}p}^{ex} = (1/2) \sigma_{pn} + \sigma^s, \quad (3.9)$$

where

$$\sigma^s = (\pi \lambda^2 / 2) \sum_J (2J+1) (1 - \eta_J)^2 \quad (3.10)$$

is the shadow scattering cross section. At present we cannot say anything definite about it except that it is small. Therefore we shall tentatively neglect it and try to compare

$$\sigma_{\bar{p}p}^{el} + \sigma_{\bar{p}p}^{ex} = (1/2) \sigma_{pn} \quad (3.11)$$

with experiment. $\sigma_{\bar{p}p}^{el} + \sigma_{\bar{p}p}^{ex}$ is given by $\sigma_{\bar{p}p}^{tot} - \sigma_{\bar{p}p}^{an}$.

At about 500 MeV, necessary data are given in Table I. Using these results, we get

a) From Chamberlain's data :

$$\sigma_{\bar{p}p}^{el} + \sigma_{\bar{p}n}^{ex} = 15 \pm 10 \text{ mb.}$$

Therefore, the agreement is satisfactory since $(1/2)\sigma_{pn} \simeq 16 \text{ mb}$ at this energy. In this case, the cut off angle is large (14° and 20°). So that his total cross section does not include shadow scattering, and the error due to the neglecting of the second term of (3.9) is $(1/2)\sigma^s$ (coming from the charge exchange scattering). We may assume that this is smaller than about 10 mb.

b) From Piccioni's total cross section and Chamberlain's annihilation cross section:

$$\sigma_{\bar{p}p}^{el} + \sigma_{\bar{p}p}^{ex} = 8 \pm 10 \text{ mb.}$$

Therefore, agreement is not so good in this case. It should be noted, however, that this result is obtained by combining data from entirely different experiments and so there can exist a difference in the normalization of the cross sections.

A more definite relation exists between the charge exchange scattering cross section in the forward direction and the neutron-proton scattering cross section. As will be seen from (3.5), the angular distribution coefficient for the charge exchange scattering contains an extra factor $(-1)^{l_1+l_2}$. Therefore, if we replace θ by $\pi-\theta$ in (2.24), we get altogether $(-1)^{L+l_1+l_2}$, which is always +1 since there exists a restriction

$$L+l_1+l_2 = \text{even}$$

in the summation over l_1 and l_2 in (3.5). Therefore, if we write $d\sigma_{\bar{p}p}^{ex}(\theta)$ as

$$d\sigma_{\bar{p}p}^{ex}(\theta) = (\lambda^2/4) \sum_{JLs} B'_{\bar{p}p}{}^{ex}(L, s) P_L(\pi-\theta) d\Omega, \quad (3.12)$$

$B'_{\bar{p}p}{}^{ex}(L, s)$ is given by

$$B'_{\bar{p}p}{}^{ex}(L, s) = (1/4) \sum_{J_1 J_2 l_1 l_2} (Z(l_1 J_1 l_2 J_2; sL))^2 \{ \sin \delta_{J_1 l_1}^s \sin \delta_{J_2 l_2}^s \cos(\delta_{J_1 l_1}^s - \delta_{J_2 l_2}^s) \\ + (1/4) (1 - \eta_{J_1}) (1 - \eta_{J_2}) - (1/2) (1 - \eta_{J_1}) \sin^2 \delta_{J_2 l_2}^s - (1/2) (1 - \eta_{J_2}) \sin^2 \delta_{J_1 l_1}^s \}. \quad (3.13)$$

The first and the second term of (3.13) are the angular distribution coefficients for (pn) and shadow scattering respectively, and the third term is their interference term. Therefore, the angular distribution for the charge exchange scattering is given by

$$d\sigma_{\bar{p}p}^{ex}(\theta) = (1/4) d\sigma_{pn}(\pi-\theta) + (1/2) d\sigma^s(\pi-\theta) - d\sigma^{int}(\pi-\theta). \quad (3.14)$$

In our case, as will be seen later, $d\sigma^s(\pi-\theta)$ collimates entirely in backward direction and $d\sigma^{int}(\pi-\theta)$ is also inappreciable at angles smaller than about 120° . (See later discussion on the angular distribution.) Therefore, the charge exchange scattering in the forward direction is related to (pn) scattering quite definitely by

$$d\sigma_{\bar{p}p}^{ex}(\theta) = (1/4) d\sigma_{pn}(\pi-\theta). \quad (3.15)$$

The cross section for the charge exchange scattering within 17° was measured by Button *et al* at 440 MeV.⁵⁾ The result is

$$\sigma_{\bar{p}p}^{ex}(\theta < 17^\circ) = 3.0 \pm 1.6 \text{ mb.} \quad (3.16)$$

On the other hand, $d\sigma_{pn}(\theta)/d\Omega$ was measured by Hartzler⁶⁾ at 400 MeV. Integrating

his result according to (3.15), we get

$$\begin{aligned}\sigma_{\bar{p}p}^{ee}(\theta < 17^\circ) &= (2\pi/4) \int_0^{\pi/2} \frac{d\sigma_{pn}(\pi-\theta)}{d\Omega} \sin\theta d\theta \\ &= 1.4 \text{ mb.}\end{aligned}\quad (3.17)$$

Again the agreement is satisfactory.*

Similar discussion can be made for $(\bar{p}n)$ scattering, too. In this case, however, available data are very poor. Therefore, we do not proceed further, and remark only that the total cross section and the angular distribution in large angles are closely related to (pp) scattering as will be seen from (3.6) and (3.8).

We shall finally make a rough estimate of various cross sections assuming a simple square well imaginary potential to describe the interaction in the state corresponding to $K=0$. The range was taken as 2.5, 3.0 and $3.5 \times (\hbar/\mu c)$ (Compton wave length of pion), and the depth was taken so that they gave 82 mb for annihilation cross section at 450 MeV. The results at 450 MeV are given in Table II.

Thus, the experimental results are reproduced by taking the range $\sim 3 \times (\hbar/\mu c)$.**

We shall also give angular distribution for the elastic and the exchange part of $(\bar{p}p)$ scattering and for the elastic part of $(\bar{p}n)$ scattering in Fig. 1 and Fig. 2.*** As it has been seen, the effect to the elastic scattering from channel corresponding to $K=0$

* If nucleonic charge independence is not assumed, $\sigma_{\bar{p}p}^{el}$, $\sigma_{\bar{p}p}^{ex}$ and $B_{\bar{p}p}^{ex}(L, s)$ are given by

$$\begin{aligned}\sigma_{\bar{p}p}^{el} &= (\pi\lambda^2/4) \sum_{Jl} (2J+1) \{ 2\eta^{s_{Jl}} \sin^2 \xi_1^{s_{Jl}} + 2\eta^{s_{Jl}} \sin^2 \xi_0^{s_{Jl}} \\ &\quad + (1 - \eta^{s_{Jl}})^2 - (\eta^{s_{Jl}})^2 \sin^2 (\xi_1^{s_{Jl}} - \xi_0^{s_{Jl}}) \}, \\ \sigma_{\bar{p}p}^{ex} &= (\pi\lambda^2/4) \sum_{Jl} (2J+1) (\eta^{s_{Jl}})^2 \sin^2 (\xi_1^{s_{Jl}} - \xi_0^{s_{Jl}}),\end{aligned}$$

and

$$\begin{aligned}B_{\bar{p}p}^{ex}(L, s) &= (1/4) \sum_{J_1} \sum_{J_2} \sum_{l_1} \sum_{l_2} (Z(l_1 J_1 l_2 J_2; sL))^2 \\ &\quad \times \{ \eta^{s_{J_1 l_1}} \eta^{s_{J_2 l_2}} \sin \xi_1^{s_{J_1 l_1}} \sin \xi_1^{s_{J_2 l_2}} \cos (\xi_1^{s_{J_1 l_1}} - \xi_1^{s_{J_2 l_2}}) \\ &\quad + \eta^{s_{J_1 l_1}} \eta^{s_{J_2 l_2}} \sin \xi_0^{s_{J_1 l_1}} \sin \xi_0^{s_{J_2 l_2}} \cos (\xi_0^{s_{J_1 l_1}} - \xi_0^{s_{J_2 l_2}}) \\ &\quad - \eta^{s_{J_1 l_1}} \eta^{s_{J_2 l_2}} \sin \xi_0^{s_{J_1 l_1}} \sin \xi_1^{s_{J_2 l_2}} \cos (\xi_0^{s_{J_1 l_1}} - \xi_1^{s_{J_2 l_2}}) \\ &\quad - \eta^{s_{J_1 l_1}} \eta^{s_{J_2 l_2}} \sin \xi_1^{s_{J_1 l_1}} \sin \xi_0^{s_{J_2 l_2}} \cos (\xi_1^{s_{J_1 l_1}} - \xi_0^{s_{J_2 l_2}}) \},\end{aligned}$$

where we neglected couplings in triplet states, and $\eta_1^{s_{Jl}}$ was assumed as equal to $\eta_0^{s_{Jl}} (= \eta^{s_{Jl}})$ for simplicity. (Definition of $\xi_1^{s_{Jl}}$ and $\eta_1^{s_{Jl}}$ is formally the same as in (2.18)). Therefore, no simple relations such as (3.9) or (3.15) exist in this case. Calculations of antinucleon-nucleon scattering without the assumption of nucleonic charge independence were made by Priets⁽⁷⁾ using second order perturbation of $p\bar{s}p\bar{s}$ meson theory, by Koba and Takeda⁽⁸⁾ assuming a black sphere model and by Ball and Chew⁽⁹⁾ assuming semi-phenomenological antinucleon-nucleon potential and replacing its core part by a black sphere.

** This range seems to be unreasonably large. This can be reduced by about factor 2 by adopting a suitable form for the potential. Into this point, however, we shall not proceed further in this paper.

*** Analogous to (3.14), the angular distribution for the elastic (pp) scattering is given by

$$d\sigma_{\bar{p}p}^{el}(\theta) = (1/4) d\sigma_{pn}(\theta) + (1/2) d\sigma^s(\theta) + d\sigma^{in}(\theta).$$

(continued to the next page)

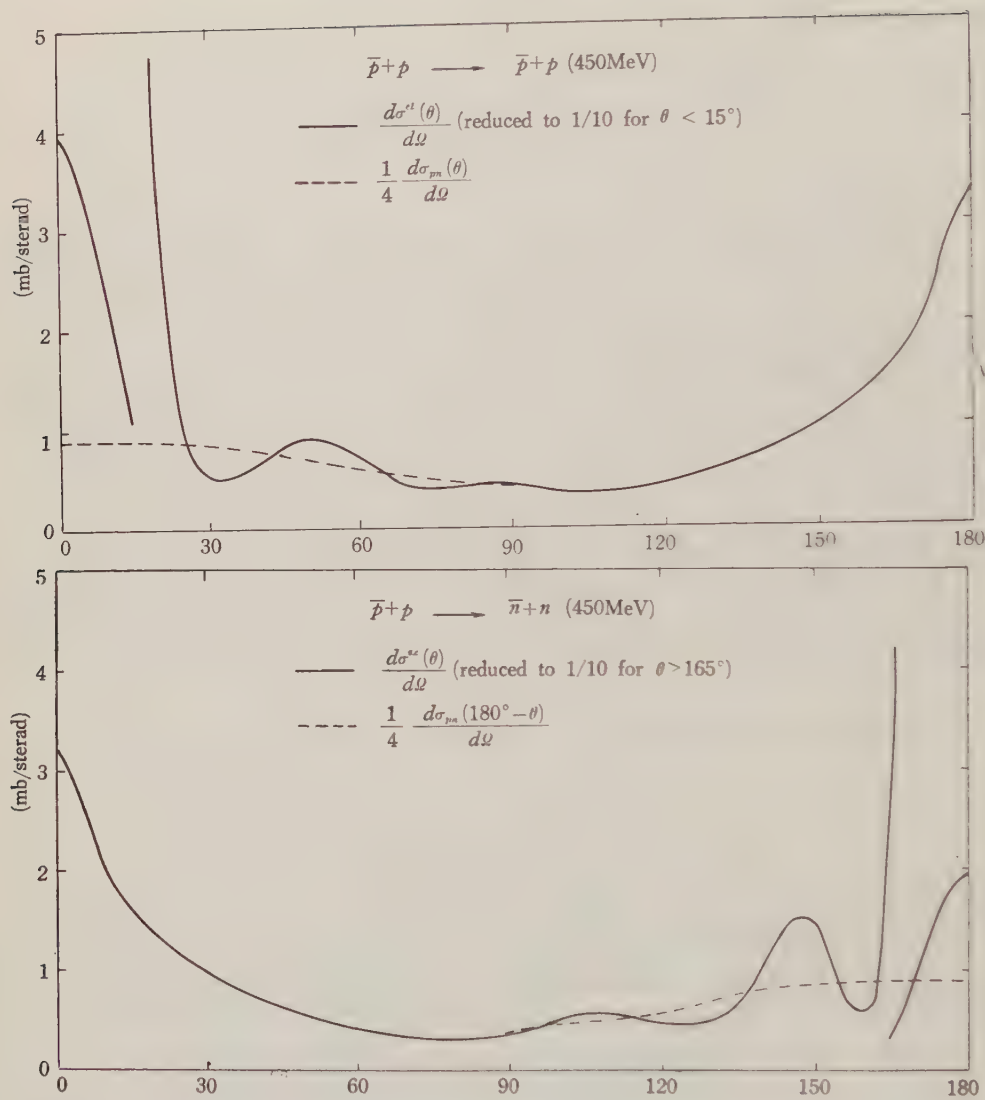


Fig. 1. The elastic scattering angular distribution curve has a forward peak which is essentially the diffraction pattern. The first minimum lies at about 25° in C.M. system. For larger angles, it is close to $(1/4) d\sigma_{pm}(\theta)/d\Omega$. In the backward hemisphere, two curves can be taken to be practically identical. The charge exchange scattering angular distribution curve has a backward peak, which comes also from diffraction pattern. In the forward hemisphere it is close to $(1/4) d\sigma_{pm}(180^\circ - \theta)/d\Omega$.

In terms of scattering amplitudes, $d\sigma^{in}(\theta)$ can be written as

$$d\sigma^{in}(\theta) = (1/8) \sum_s \sum_{m_s} \sum_{m_s'} \text{Re} \{ q^{(pn)}_{m_s'; m_s}{}^* (\theta\varphi) \cdot q^{(d)}_{m_s'; m_s} (\theta\varphi) \} d\Omega, \quad (\text{A} \cdot 1)$$

where $q^{(pn)}_{m_s'; m_s}(\theta\varphi)$ and $q^{(d)}_{m_s'; m_s}(\theta\varphi)$ are given by

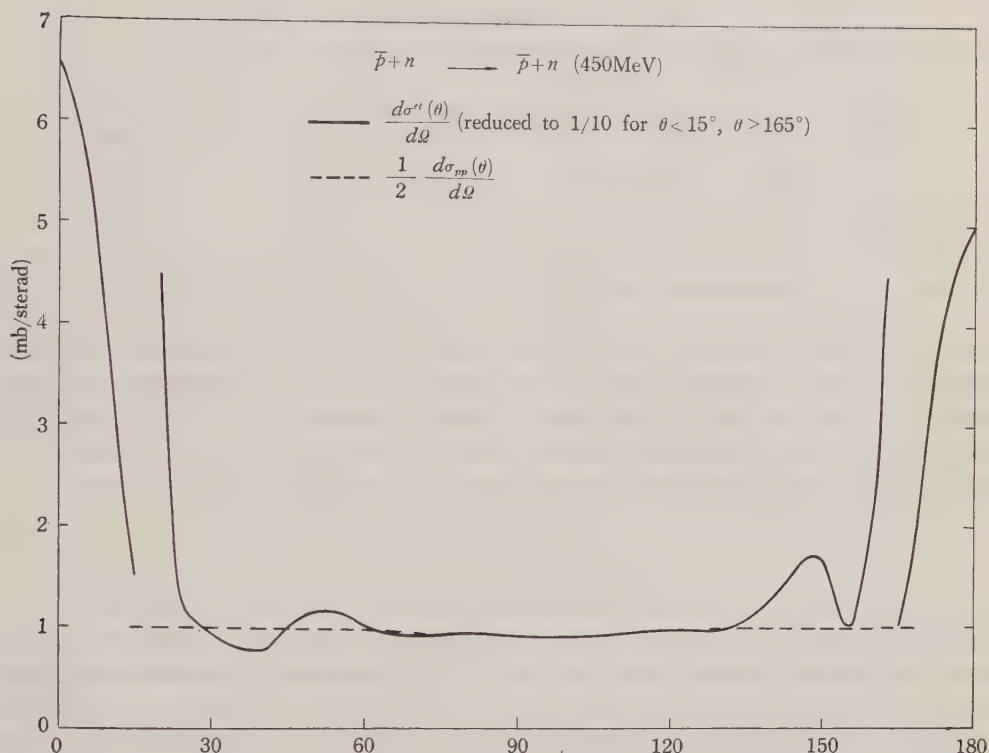


Fig. 2 The elastic scattering angular distribution curve has two peaks in forward and backward directions. Both are essentially the diffraction patterns, and small asymmetry with respect to 90° is due to the admixture of $(\bar{p}p)$ scattering contributions. Between the two minima (about 30° and 150°) the contribution from diffraction patterns is negligible, and the curve is given approximately by $(1/2) d\sigma_{pp}(\theta)/d\Omega$.

almost vanishes at angles larger than about 60° (corresponding to 30° in the laboratory system). Therefore, it is expected that at these angles the angular distribution for the elastic part of $(\bar{p}p)$ or $(\bar{p}n)$ scattering will agree with those for (pn) and (pp)

$$q^{(pn)}_{m_s'; m_s}(\theta\varphi) = \sum_J \sum_M \sum_l \sum_{m_l} \sqrt{\pi(2l+1)} C_{ls}(JM; 0m_s) C_{ls}(JM; m_l m_s') (1 - S_{ls}) Y_{lm_l}(\theta\varphi),$$

and

$$q^{(d)}_{m_s'; m_s}(\theta\varphi) = \sum_J \sum_M \sum_l \sum_{m_l} \sqrt{\pi(2l+1)} C_{ls}(JM; 0m_s) C_{ls}(JM; m_l m_s') (1 - \eta_J) Y_{lm_l}(\theta\varphi) \\ = \sum \delta m_s, m_s' q^{(d)}(\theta).$$

Here $q^{(d)}(\theta)$ falls off rapidly to zero, while $q^{(pn)}_{m_s'; m_s}(\theta\varphi)$ varies relatively slowly in this region. Therefore, we can approximate $q^{(pn)}_{m_s'; m_s}(\theta\varphi)$ by $q^{(pn)}_{m_s'; m_s}(0\varphi)$ in (A.1). Then, (A.1) can be written as

$$d\sigma^{in}(\theta) = (1/8\pi) \sigma_{pn} q^{(d)}(\theta) d\Omega. \quad (\text{A.2})$$

In this approximation, therefore, we can avoid the explicit use of δ^s_{Jl} . Fig. 1 and Fig. 2 are written in this way. $q^{(d)}(\theta)$ was calculated assuming imaginary potential with range $3 \times (\hbar/\mu c)$ (the second column in Table II). $d\sigma_{pp}(\theta)$ was assumed to be isotropic for all angles.

Table II.

Range ($\hbar/\mu c$)	2.5	3.0	3.5
σ 's (mb)			
$\sigma_{\bar{p}p}^{e\bar{l}}$	16.5	13.6	11.9
$\sigma_{\bar{p}p}^{e\gamma_1}$	82	82	82
$\sigma_{\bar{p}p}^{e\pi}$	12.1	10.2	9.1
$\sigma_{\bar{p}n}^{e\bar{l}}$	25.0	20.3	17.4
$\sigma_{\bar{p}n}^{e\gamma_1}$	82	82	82

respectively. Especially, in the case of ($\bar{p}n$) scattering, coexistence of partial waves with different parities in channels specified by the definite value of K is forbidden by the Pauli principle. Thus, the angular distribution becomes symmetrical with respect to 90° **. These are important conclusions from the assumption of nucleonic charge independence, and the validity of this assumption may be checked by examining these predictions.

§ 4. Concluding remarks

As pointed out in § 3, we must take the range of annihilation approximately 1.2 times larger than usually assumed if nucleonic charge independence is assumed. In this point, the situation becomes worse, since this range is considered to be unreasonably large even in the usual theory.** It gives, however, simple relations between the elastic and the charge exchange parts of the antinucleon-nucleon scattering and the nucleon-nucleon scattering, and also definite predictions for the angular distributions. Unfortunately, these results are based on the assumption that $\tilde{\epsilon}_{\alpha\beta}$'s are negligible as compared with $\tilde{\sigma}_{\alpha\beta}$'s. At present there is no means to check the validity of this assumption, and they cannot avoid corresponding ambiguities.*** Nevertheless, it would be of some interest to investigate them further experimentally as a trial of finding a new method of analyzing antinucleon-nucleon interaction.

In conclusion, the authors wish to thank Prof. Owen Chamberlain for suggesting this calculation.

[†] Strictly speaking, contributions from channels corresponding to $K=0$ and 1 can interfere. But this effect is not so appreciable since their angular distributions are very different.

** Levy showed⁽¹⁰⁾ that, using intermediate coupling theory, the range of the imaginary part of the antinucleon-nucleon potential can be considerably large, of the order of ($\hbar/\mu c$). It should also be noted⁽¹¹⁾ that the assumption of nucleonic charge independence leads to non-local pion-nucleon interaction automatically.

^{†††} Backward peak of the charge exchange scattering in (pp) scattering and the symmetry with respect to 90° in ($\bar{p}n$) scattering is comparatively free from this ambiguity. Therefore, these features will be especially suitable to check our assumptions.

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Letters to the Editor

The opinions expressed in these columns do not necessarily reflect those of the Board of Editors. Communications should be submitted in duplicate and should be held to within 100 lines (pica type) on standard size letter paper (approx. 21×30cm.), so that each letter will be arranged into two pages when printed. Do not forget to count in enough space for formulas, figures or tables.

Rigidity for Octupole Type Surface Deformation and Shell Structure

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May 6, 1958

In certain regions of elements, the even-even nuclei have been found to possess rather low lying states of odd parity. These states have been observed in α -decay spectrum and the ratio of gamma-transition probabilities to 0^+ and 2^+ states of the heavy elements near $Z \sim 90$ and $N \sim 136$.¹⁾ Low lying odd parity levels have also been found in the even-even nuclei in the rare earth region; e. g., the lifetime of 1^- state of $^{152}_{62}\text{Sm}$ is a factor 150 longer than a single proton estimate.²⁾ This region is related with $Z \sim 60$ and $N \sim 90$. The systematic occurrences of these low lying odd parity levels suggest that they may represent collective oscillations of octupole type. Some of the qualitative properties of octupole type oscillations of a nuclear surface have already been discussed by Copenhagen group.³⁾ Bohr and Mottelson have estimated the electric dipole transitions and attempted to obtain information on the

nuclear octupole distortion.⁴⁾ Recently, Lee and Inglis have calculated the energy change associated with pear-shaped deformation using the nucleon wave functions of a spheroidal harmonic oscillator potential.⁵⁾ They found that this energy change is always positive but could not examine shell structure dependence of the octupole deformation because of neglect of a spin-orbit coupling.

In addition to above mentioned two regions, the octupole type surface deformation of a subshell of nucleon number 40 may also be large. The E3-transitions of j -forbidden type occur in neutron or proton number 43, 45 and 47, and are transitions between $(7/2^+)$ state and $(1/2^-)$ state. This may suggest that the surface rigidity for octupole type deformation of this subshell is very small. According to Sano's calculation, main contributions to transition of this type come from configuration mixing and contributions from collective transitions of octupole type have only minor effects.⁶⁾ Therefore, behavior of the surface rigidity for octupole type of deformation in the subshell of nucleon number 40 is very interesting for us.

We have calculated the surface rigidity C_3 of closed shells for an octupole type of surface deformation using almost the same method as that of Marumori, Suekane and Yamamoto.⁷⁾ In our case, the Moskowski's coordinates transformation can-

not be used, and we introduce another more general coordinates transformation which transforms a deformed surface into spherical one. Of course, the results of calculations for C_2 (the rigidity for quadrupole type of surface deformation) are equal in these two transformations. We include a spin-orbit coupling in our calculation and, for simplicity, neglect the

effects of Coulomb interactions.

The results of our calculations are shown in Fig. 1. The calculated values of C_3 are very small in the neighbourhood of subshells of nucleon number 32, 40, 56, 64, 82 and 90. The nucleus which has several nucleons in the next subshells of these subshells may be easily deformable for octupole type of deformation. This

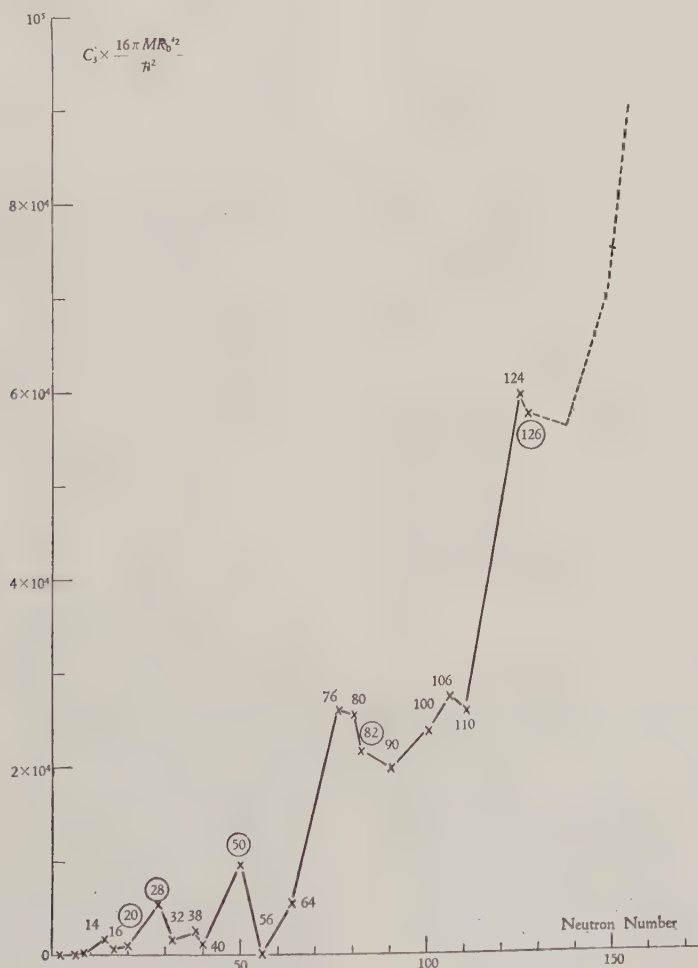


Fig. 1. The surface rigidities of neutron cores, C_3 . In this figure, $R_0' = R_0 + \lambda_0$, $\lambda_0 = (\hbar^2/MV_0)^{1/2}$, where R_0 is the nuclear radius and V_0 is the depth of the potential. In the regions between two closed shells, the rigidity may be reduced very much because of the crossing of the particle levels due to the large deformation of the core which is caused by coupling of the core and extra-particles.

shell structure dependence of C_3 is in fairly good agreement with the trend of above mentioned experimental evidences except for the subshell of nucleon number 32. Especially, the smallness of the rigidity of the subshell of nucleon number 40 may suggest that the above mentioned explanation of j -forbidden type E3-transitions may be correct. According to our calculation, the rigidity of the subshell of nucleon number 32 is also very small. Therefore, we can expect some effect of the octupole type of collective oscillation in this region, but we have no experimental information. Our results for nucleon number larger than about 100 are not so reliable, because of the lack of accurate knowledge about the level orderings and their distances of shell model to above region of this nucleon number. In this calculation, we used Klinkenberg's level scheme up to $3d_{3/2}$ -level. Smaller values of C_3 or more pronounced shell structure dependent behavior are expected by the perturbation from $1j$ (and higher odd parity) levels to $2g$ and $1i$ levels and this may correspond to the region of $N \sim 90$ and ~ 136 .

The full paper of this work will be published in near future. Preliminary report of this work will be read at the second International Conference on the Peaceful Uses of Atomic Energy at Geneva. In this report, we have not been able to find a strong shell structure dependence of C_3 such as Fig. 1, because of unsuitable approximation used in the calculation.

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Stellar Syntheses of the α -Particle Nuclei heavier than Ne^{20}

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May 26, 1958

Many authors¹⁻³⁾ have discussed the nuclear reactions which can go on in stellar interiors up to the point at which the helium has been exhausted by the $3\alpha \rightarrow \text{C}^{12}$ and subsequent (α, γ) reactions. Beyond this stage stars contract again and heat up until further thermonuclear reactions begin to occur inside their cores. To explain the cosmical abundances of α -particle nuclei, Mg^{24} , Si^{28} , S^{32} , A^{36} , and Ca^{40} , Burbidge, Burbidge, Fowler and Hoyle⁴⁾ proposed the so-called α -process. The first and most important reaction in this process is $\text{Ne}^{20}(\gamma, \alpha)\text{O}^{16}$ due to its small negative Q -value. Once α -particles have been emitted, the nuclei heavier than

Ne^{20} can be built by successive (α, γ) reactions. In very hot stars consisting of C^{12} , O^{16} and Ne^{20} , ion-ion reactions, such as $\text{C}^{12} + \text{C}^{12} \rightarrow \text{Ne}^{20} + \alpha$ and $\text{C}^{12} + \text{O}^{16} \rightarrow \text{Mg}^{24} + \alpha$, must also be taken into account as a possible α -particle source.

The purpose of this note is to investigate the stellar conditions, that is, the temperature, the density and the duration of time which are necessary to explain the observed abundances of α -particle nuclei by the above process. Before doing this, various nuclear reaction rates were calculated by the well-known procedures.⁴⁾ In calculating the (α, γ) reaction rates for the nuclei heavier than Mg^{24} , their atomic number dependence being the most important for our purpose, we can use the approxi-

mate cross sections given by the statistical theory, because in such reactions excitation energies are so high that the resonant properties of individual levels are smeared out. Fig. 1 gives the reaction times for various nuclear reactions as functions of temperature.

(i) *Equilibrium theory*

To explain the abundances of α -particle nuclei heavier than Ne^{20} by the equilibrium theory, the temperature $\sim 10^{10} \text{ }^\circ\text{K}$ and the matter density $\sim 5 \times 10^8 \text{ g/cm}^3$ are required. Under this condition the nuclear reaction times are of the order of 10^{-5} sec and it seems rather unlikely that we can find stellar outbursts which are rapid enough to assure the freezing-in of this established equilibrium.

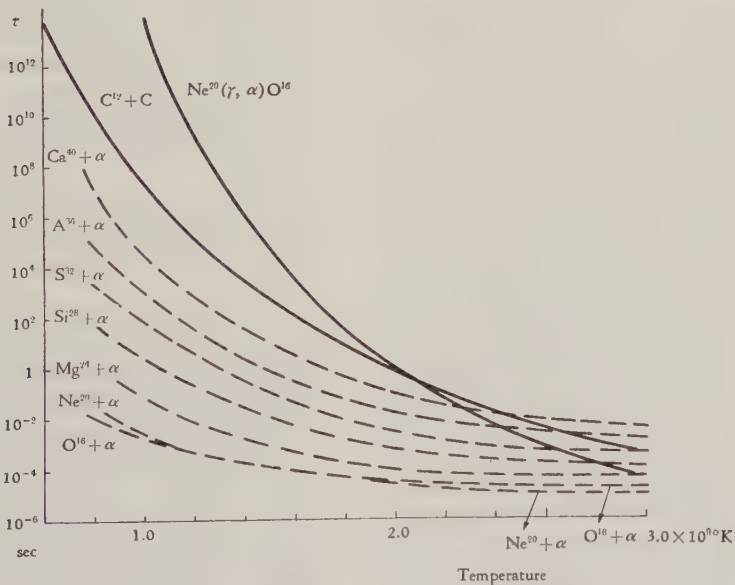


Fig. 1. The solid curves refer to the reaction times τ (in sec), plotted against temperature T , while the dotted ones refer to the mean lifetimes of α -particles for (α, γ) reactions, the density of target nuclei being taken as 10^5 g/cm^3 .

(ii) *Slow syntheses in stellar cores*

The fastest ion-ion reaction, $C^{12} + C^{12}$, competes with $Ne^{20}(\gamma, \alpha)O^{16}$ at the temperature $T \lesssim 2 \times 10^9$ °K with the density $\rho \simeq 10^5$ g/cm³.⁵⁾ When the central temperature of stars consisting of C^{12} , O^{16} and Ne^{20} with the above density rises to about $6 \sim 7 \times 10^8$ °K, $C^{12} + C^{12}$ reaction can be a main energy source of these stars with 100~1000 times solar luminosities. At this temperature, however, the atomic number dependence of the (α, γ) reaction rates are too large to reproduce the cosmical abundances of α -particle nuclei heavier than Si^{28} .

Alternatively, if the stellar cores consist of Ne^{20} only,³⁾ $Ne^{20}(\gamma, \alpha)O^{16}$ is a main α -particle source for the formation of the heavier nuclei. If $Ne^{20}(\gamma, \alpha)O^{16}$ and subsequent (α, γ) reactions are to be the energy sources of such stars, the central temperature near 1×10^9 °K is required. This temperature is still too low to overcome the above difficulty.

(iii) *Rapid syntheses in the supernovae explosions*

At higher temperature $T = 2 \sim 3 \times 10^9$ °K, the differences among the (α, γ) reaction rates become so small that it will be possible to explain the abundances concerned in terms of the α -process.

At $\rho = 10^5$ g/cm³ where the (α, γ) reaction rates are much greater than (γ, α) ones, the emitted α -particles are absorbed instantaneously by C^{12} , O^{16} or Ne^{20} , but they are hardly used for the formation of nuclei heavier than Si^{28} . The result is not different from the case (ii).

Our calculations, however, show that the abundances in question can be reproduced by taking the density $\rho \simeq 10^2$ gm/cm³, where the (γ, α) reaction rates are com-

parable to (α, γ) ones. At this temperature the reaction time for $Ne^{20}(\gamma, \alpha)O^{16}$ is $10^{-2} \sim 1$ sec, while $10^3 \sim 10^7$ sec for the other (γ, α) reactions, and to explain the observed abundances it is necessary for such temperature to continue for a rather short time, $1 \sim 10^2$ sec, with a rapid heating-up and a subsequent cooling. Such stellar conditions could be realized in the supernova explosions, as the time scale of implosion preceding the explosions is estimated to be of the order of 10^{-1} sec⁴⁾ and such high temperature will continue for $1 \sim 10^2$ sec.

The details of this note will soon appear in this journal.

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The Global Symmetry of Pion-Baryon Interactions and Bound States of Hyperon-Nucleon System

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May 20, 1958

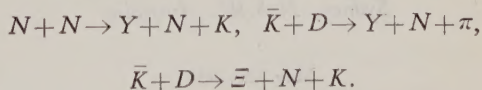
Following Gell-Mann¹⁾ we shall assume

the global symmetry of the pion-baryon interactions in the iso-space (all coupling constants in the interactions are equal). We shall see here what follows about the hyperon (Y)-nucleon (N) forces from this assumption. If one also neglects mass differences among baryons; one obtains $Y-N$ forces due to the pion-exchange immediately from the knowledge about $N-N$ forces.²⁾ Particularly, one sees that the identities

$$\begin{aligned} V_{\pi}\left(\frac{\Lambda^0 - \varepsilon^0}{\sqrt{2}}, N\right) &= V_{\pi}(\Sigma^-, N) \\ &= V_{\pi}(\Xi^-, N) = V_{\pi}(n, N), \\ V_{\pi}\left(\frac{\Lambda^0 + \varepsilon^0}{\sqrt{2}}, N\right) &= V_{\pi}(\Sigma^+, N) \\ &= V_{\pi}(\Xi^0, N) = V_{\pi}(p, N), \end{aligned}$$

where $V_{\pi}(X, N)$ means the force between X and N due to the pion exchange and n and p stand for a neutron and a proton, respectively (care must be taken here with reference to the exclusion principle). The remaining part $\delta V(Y, N)$ of the $Y-N$ force consists of two contributions, the one due to mass differences ΔM among baryons and the other caused by the K -meson exchange.³⁾ The former would be of the order of $\Delta M/M$ as compared to $V_{\pi}(Y, N)$, M being the baryon mass. The latter is considered relatively unimportant because of either or both of the following two reasons; (a) All K -meson baryon interactions may be 'moderately' strong while the global pion interactions are very strong. (b) If one assumes the existence of a hard core with radius $\sim 1/3 m_{\pi}$ (m_{π} pion mass) for all baryon pairs, major part of K -meson exchange forces would be masked by this hard-core. Thus one may arrive

at an approximate means to treat the two baryon problem. In the Schrödinger equation the empirical reduced mass is used and the potential $V(Y, N)$ is approximated by $V_{\pi}(Y, N)$ (plus a hard core). In this simplified situation it is extremely simple to survey the possibility of bound states. It turns out that $\Sigma^- - n$, $\Xi^0 - p$ and $\Xi^- - n$ have bound states in the ^1S state with binding energies ~ 0.06 , ~ 0.2 and ~ 0.2 Mev, respectively. All other cases fail to form any bound states. Note that two neutrons cannot form any bound states while the above cases can. This is because the $Y-N$ system has larger reduced mass than the $N-N$ system. In this simplified case there are no bound states of $\Sigma^+ - p$ because of the Coulomb repulsion. However, if $\delta V(\Sigma^+, N)$ gives rise to an attractive force which is effectively $\gtrsim 10\%$ of $V_{\pi}(\Sigma^+, N)$,⁴⁾ then a bound $\Sigma^+ - p$ state is now possible. There is one example reported so far which could be a bound $\Sigma^+ - p$.⁵⁾ If our approximation $V(Y, N) \approx V_{\pi}(Y, N)$ is reasonably good as we have suspected above, the binding energies of all bound $Y-N$ states are very small.⁶⁾ As is well known, the smaller the binding energy the larger the scattering length. One can expect quite an appreciable effect of the final state interaction between two baryons in the processes like



The energy distribution of the final mesons is mainly determined by the scattering length of the accompanying baryon pairs,⁷⁾ and gives a way to test whether our expectation about nuclear forces is really the case or not.

- 1) M. Gell-Mann, Phys. Rev., **106** (1957) 1296. The baryons are assumed to be spin $1/2$.
- 2) See Supplement of Prog. Theor. Phys., No. 3 (1956).
- 3) The $Y-N$ forces were studied by many people, Nishijima, Iwao, Wentzel, Konuma, Lichtenberg and Ross and others. Also see Dalitz, to be published.
- 4) In term of the well depth parameter s , $s \approx 1.06$ for $V_\pi(\Sigma^+, p)$. If $V_\pi(\Sigma^+, p) + \delta V(\Sigma^+, p)$ has $s \geq 1.16$, bound $\Sigma^+ - p$ can exist.
- 5) H. Huzita et al., Nuovo Cim.
- 6) The emission of the hyperdeuteron (i. e., bound $Y-N$ system) from nuclei can be considered as a pick up process of a nucleon by an hyperon. The probability of such pick up process is roughly proportional to $\sqrt{B}$, if $B \leq 2$ Mev, where B is the binding energy of the hyperdeuteron. If the hyperdeuteron emission is really rare event, B is very small or the hyperdeuteron does not exist.
- 7) Y. Fujimoto and Y. Yamaguchi, Prog. Theor. Phys. **6** (1951), 166.
A. Pais and others, to be published.

A Note on the Specification of Nuclear Potentials

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In phenomenological studies of nuclear forces the specification of the strength and range of the potential in terms of the

well-depth parameter s and the intrinsic range b , as defined by Blatt and Jackson,¹⁾ has been used frequently. Expressions for Gaussian, Exponential and Yukawa wells are given in eqs. (4.4) and (4.5) of BJ. The numerical constants in those formulae were determined by means of numerical integrations of the Schrödinger equations for zero energy. With a fast computer more accurate numerical constants for all three types of potential have now been computed and are reported here. These new constants should replace those given in BJ.

In the notations of BJ we write $(W(r) = -(M/\hbar^2)V(r))$:

Gaussian well :

$$W(r) = sGb^{-2} \exp[-K(r/b)^2]$$

Exponential well :

$$W(r) = sGb^{-2} \exp[-K(r/b)]$$

Yukawa well :

$$W(r) = sGb^{-2} \exp[-K(r/b)](r/b)^{-1}$$

In Table I we give the numerical values of constants G and K for these three types of potential. We have also given (in brackets) the values of BJ for comparison.

If the potentials are specified as

Gaussian well :

$$V(r) = -V_0 \exp[-(r/\beta)^2]$$

Exponential well :

$$V(r) = -V_0 \exp[-2r/\beta]$$

Yukawa well :

$$V(r) = -V_0 \exp[-r/\beta]/(r/\beta),$$

one has

$$s = CMV_0\beta^2/\hbar^2 \text{ and } b = D\beta$$

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with M =nucleon mass and C and D numerical constants depending on types of the potential. In Table II we have given the values of these constants together with

Table I

	G	K
Gaussian	5.528703 (5.5296)	2.059871 (2.0604)
Exponential	18.126198 (18.1301)	3.540787 (3.5412)
Yukawa	3.561319 (3.5605)	2.120060 (2.1199)

Table II

	C	D
Gaussian	0.3725776 (0.37261)	1.435225 (1.4354)
Exponential	0.1729151 (0.17291)	1.770393 (1.7706)
Yukawa	0.5953017 (0.59531)	2.120060 (2.1196)

the values of Blatt and Weisskopf²⁾ in brackets.

As a check on these numbers, the values of K and G for the exponential well have been computed from the well-known analytic solution.³⁾ These values agree with the numerically computed values to 8 significant figures in G and 7 significant figures in K .

The writer expresses his sincere thanks to Professor H. Messel for his hospitality and to Dr. J. M. Blatt for many valuable suggestions and continuous encouragement throughout the present work.

- 1) J. M. Blatt and J. D. Jackson, *Phys. Rev.* **76** (1949), 18, referred to as BJ in the present note.
- 2) J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics*, John Wiley and Sons, New York, 1952, p. 55.
- 3) H. A. Bethe and R. F. Bacher, *Rev. Mod. Phys.* **8** (1936), 82.

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